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ADSORPTION OF HYDANTOINS ON ACTIVATED CARBON

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Abstract

A carbon adsorption study was performed using hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin as solutes. The study included single solute batch kinetic tests to determine the required elapsed time for each solute to reach solution equilibrium with Filtrasorb 400 activated carbon. Single solute isotherm tests were performed to establish X/m values (amount of solute adsorbed/unit weight of carbon) for various solution equilibrium concentrations. Multisolute isotherm points were utilized to determine the relative order of adsorption strength on the activated carbon. It was determined that adsorption of the three solutes followed the order: 5-ethyl-5-methylhydantoin > 5,5-dimethylhydantoin > hydantoin. Adsorption column tests were performed for single solute, bisolute, and trisolute solutions as well as an undiluted coal gasification wastewater containing predominantly hydantoin compounds. The column adsorption studies in concert with the isotherm studies demonstrated that activated carbon has low adsorption capacity for hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin. Adsorption using activated carbon did not appear to be an effective treatment process for the removal of hydantoins from the coal gasification wastewater.

1. Introduction.

Carbon has been used for water purification by mankind since 200 B.C., but its adsorptive properties were not discovered until much later. In 1773, the German chemist Karl Wilhelm Scheele definitively demonstrated the ability of carbon to adsorb gases (Miller, 1980). In 1785, the ability of carbon to remove organically derived colors from solution was discovered by another German chemist, Johann Tobiss Lowitz (Miller, 1980). The first major industrial useage occurred during World War I when the Allies used activated carbon in the filters of gas masks to protect against chlorine gas (Miller, 1980). Since that time, activated carbon has been used extensively by the food and beverage industry as well as in water purification and wastewater treatment processes to remove tastes, odors, colors, and organic impurities from solution.

In a wastewater treatment process design in which activated carbon is viewed as a prospective alternative, typically batch kinetic studies, adsorption isotherm studies, and column studies are performed on a bench-scale to determine the adsorption kinetics of the system. Once the adsorption kinetics are characterized, a mathematical model can be developed to substantially predict the adsorptive capabilities of the carbon for the solute at various concentrations and flow rates for a carbon contacting

system. A pilot plant can be designed based upon the model and kinetic data, which operated under field conditions similar to the full-scale treatment process, can provide data to design and operate the full-scale carbon contacting system.

Activated carbon is often used as a contact medium for biological treatment systems since it has the excellent characteristics of being lightweight, having a large surface area, a large void volume, and surface properties that are conducive to the growth of microorganisms (Normann and Frostell, 1977). The activated carbon may also adsorb inhibitors to microbe metabolism which would allow the biological treatment process to continue even though inhibitory agents are present in the waste stream. In this regard, it is particularly useful as a medium for anaerobic filters since anaerobic treatment processes are relatively sensitive to inhibition. At the present time, anaerobic filters are being studied as a treatment alternative for the water quench waste stream from a pilot-scale coal gasifier operated by the University of North Dakota Energy Research Center (UNDERC) (Willson, et al., 1983). The UNDERC gasifier is in a commercial dry-ash, slagging fixed-bed configuration. Coal is gravity fed from hoppers at the top of the gasifier, and is combusted and gasified by a countercurrent flow of hot gases. An oxygen/steam mixture is introduced at four tuyeres positioned above the hearth. Ashes exit the bottom of the furnace while hot product

gases, devolitalization products and steam exit the top of the gasifier at approximately 325°F. The hot gases enter a spray cooler or water quenching vessel where recycled gas liquors mixing with the gas stream removes soluble gases and devolitalization products. The soluble gases removed include NH_3, CO_2, HCN, and H_2S while the devolitalization products include tars, oils, and water vapor. The product gas then is processed through an overhead gas cooler where additional light oils and water vapor are removed.

The wastewater streams in the gasification process are the gas liquors from the spray cooler and light oils and water vapor from the overhead gas cooler. Both streams are sent to a tar/oil/water separator where oils and tar are gravity separated. The wastewater stream is then gravel filtered to remove residual tars and passed through a solvent extraction column for the removal of phenol. The solvent used is diisopropyl ether. The solvent-extracted wastewater is then heated through a heat exchanger to 190°F to 200°F and introduced to a stripping tower. A counterflow of steam removes ammonia and acid gases from the wastewater. The solvent-extracted, ammonia-stripped wastewater now has the following characteristics (Willson, et al., 1983):

Table 1. Wastewater Characteristics

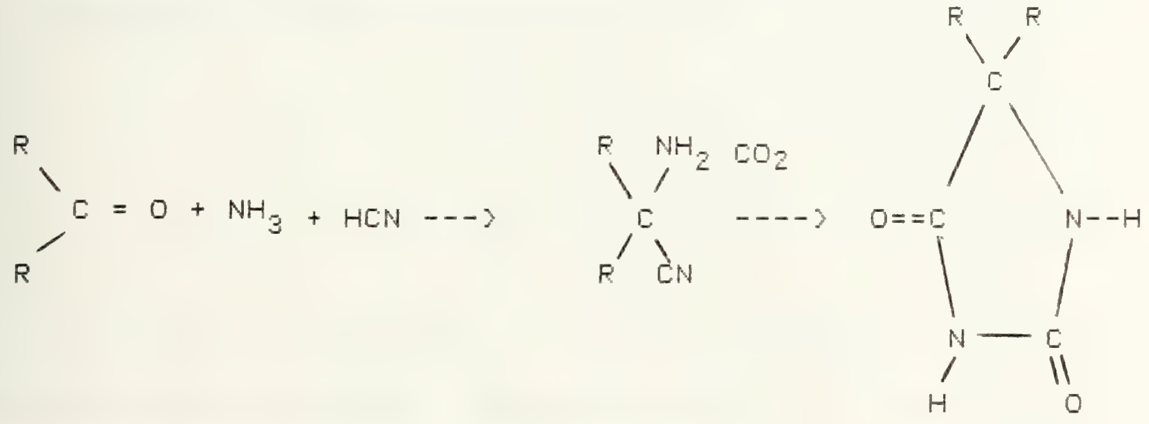
alcohols	230 mg/l
phenols	160 mg/l
hydantoins	2600 mg/l
COD	5700 mg/l
ammonia	560 mg/l
pH	8.9
alkalinity	1500 mg/l
methanol	230 mg/l

The concentration of hydantoins was unaffected by the solvent extraction and ammonia stripping.

Prior to introducing the waste stream to the anaerobic filter, it is diluted ten times and the carbon bed is operated in the expanded mode using recycled filter effluent. This dilutes the waste sufficiently to allow the slow-growing anaerobes to metabolize the waste constituents and prevents a shock loading of the filter. The anaerobic filters initially remove substantial amounts of COD, but are soon inhibited due to toxic constituents in the waste stream. It is possible that the activated carbon which makes up the contact medium for the anaerobes is adsorbing the toxic inhibitors during the initial stages of COD removal, and upon carbon exhaustion, the inhibitors are no longer removed

from the waste stream and produces inhibitory or toxic effects on the anaerobic bacteria in the filter.

From Table 1, the waste component in highest concentration is hydantoin at 2600 mg/l. Of the 2600 mg/l, 5,5-dimethylhydantoin makes up approximately 2100 mg/l and 5-ethyl-5-methylhydantoin is 500 mg/l (Willson, et al., 1983). The hydantoins are not primary devolatilization products, but are formed during water quenching and tar-oil separation from the reaction of ketones, cyanides, ammonia, and carbon dioxide by the following reaction (Willson,et al.,1983):



Hydantoins are not easily degraded by either chemical or biological means (Willson, et al., 1983), and could possibly inhibit anaerobic metabolism. Should the anaerobic filter effluent be used as cooling tower makeup water, the hydantoins must be removed to prevent adverse effects on the performance of the heat

exchanger in terms of dissolved solids and possible fouling of the heat exchanger surfaces. Also, the environmental effects of hydantoins being discharged into the environment are essentially unknown at the present time.

The objective of this research was to determine the adsorption kinetics of hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5--methylhydantoin from water through the use of batch kinetic tests, single, bisolute and trisolute isotherms and column studies. Also, a column study was performed with undiluted coal gasification wastewater which had been solvent extracted and ammonia stripped to determine carbon's effectiveness as a treatment process for the undiluted stream.

2. Literature Review.

Adsorption from aqueous solution is a system consisting of three parts, the adsorbent, the adsorbate, and the solution. The properties of each component of the system affects the overall amount of adsorption of adsorbate that can occur. The adsorbent used was activated carbon, the adsorbates used were hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin, and the solvent used was distilled deionized water in most cases.

Adsorbent. Activated carbon is produced from charring raw materials such as coal, wood, coconut shells, oil, sugar or other carbonaceous materials by carbonization and activation processes. During carbonization, the char is formed by slowly heating the raw materials to temperatures usually up to 600°C. in the absence of air, and additions such as calcium chloride, magnesium chloride, and zinc chloride may be added to catalyze the process or to impart certain properties in the final activated carbon (Hassler, 1963). Once heated, the char is "activated" by exposure to oxidizing gases such as carbon dioxide, steam, or air. The activation process "burns out" readily oxidizable materials to form micropores and macropores within the individual char particle (Mattson and Mark, 1971). The formation of micropores and macropores provides the large internal surface area typical of the activated carbon particle.

During activation, the remaining solid portion of the carbon particle is formed into microcrystallites of carbon. Microcrystallites are structures of fused and turbostratically arranged carbon rings. The carbon rings are hexagonal in shape and are flat or in the form of planes.. The diameter of the planes are from 20 to 50 angstroms, and are turbostratically arranged due to various functional groups at the edge of the basal planes forming bonds of various configurations between adjacent planes. These functional groups consist commonly of carboxyl, phenolic, and

quinone groups, and sometimes include normal and flourescein-type lactones, carboxylic acid anhydrides, and cyclic peroxides (Mattson and Mark, 1971). Hennig (1965) employed electron microscopy to prove that the edges of the basal planes were the most reactive sites (Mattson and Mark, 1971). Measuring the quantities of surface oxides formed before and after cleaving a graphite crystal five times, he determined that the amount of surface oxides formed did not change. Since the area of the basal planes was increased by a factor of six and the edge surface areas remained constant, Hennig concluded that that the oxygen reacts with the crystallite edges only. The micropores are formed by the burnout of individual microcrystallite planes. The burnout that occurs is enhanced by the vacancies that occur due to the removal of volatile materials during carbonization. The diameter of the micropore is generally <100 angstroms while the diameter of the macropores is greater than 100 angstroms. The walls of the micropore makes up the majority of the surface area available within the carbon particle (Snoeyink and Weber, 1967).

Carbonization and activation temperature plays a key role in the final size of the microcrystallite and defines the particular functional group that can be expected to be found on the surface of the carbon particle. As the activation temperature increases, the size of the microcrystallite tends to increase. Puri (1974) determined that by outgassing a carbon at 600° C, he virtually

eliminated acidic CO_2-complexes leaving only CO-complexes on the surface of the carbon. Outgassing at 1000°C eliminated the CO-complexes leaving the carbon virtually oxygen free. Using the outgassed carbons in adsorption isotherms with phenol, Puri determined that the carbon outgassed at 600°C having predominantly CO-complexes was a better adsorbent the carbon (outgassed at 1000°C) having virtually no oxygen complexes (Puri, 1974). Obviously, activation temperature bears an important role in determining the surface characteristics and eventual adsorption properties of the activated carbon.

Some carbons may have large percentages of oxygen, hydrogen and inorganic ash chemically adsorbed on the surface which would affect the carbon's overall adsorption characteristics.

Oxygen complexes affect the adsorptive properties of the carbon by altering the polarity of the carbon surface. The carbon surface tends to have less adsorption capacity for non-polar adsorbates when oxygen surface complexes are present, and increased adsorption capacity for polar adsorates. Also, adsorbates that have a tendency to combine with oxygen are more readily adsorbed than those adsorbates that do not (Snoeyink and Weber, 1967). Oxygen may appear on the carbon surface by three means: the starting material contains oxygen which remains stable during the carbonization and activation processes, oxygen may be physically adsorbed by carbon at room temperatures while in

contact with air, and oxygen may be chemically adsorbed during activation by oxidizing agents. Once formed by whatever means, the oxygen complexes (CO and CO_2 complexes) are extremely stable and can only be removed by degassing at very high temperatures (Puri, 1975). The heat of adsorption for oxygen on activated carbon at 20°C is initially about 100-110 kcal/mole (Mattson and Mark, 1971).

Hydrogen may be found as terminal groups attached to the hydrocarbon planes of the microcrystallite or as a part of functional groups attached to the planes. The amount of inorganic ash found on the carbon surface is a function of the inorganic constituents of the starting material and the inorganic salts used to catalyze the carbonization process, or used to cause selective adsorption in the final activated carbon. The selective adsorption may be due to complex formation, ion-pair formation, precipitation reactions and oxidation-reduction reactions with the adsorbate in solution.

Carbons can be classified by their acid-base adsorption characteristics. Carbons activated at temperatures of approximately 400°C will adsorb base and are classified as L-carbons. Those carbons that are activated at temperatures of 800°C to 1000°C and will adsorb acid are H-carbons. Therefore, H-carbons will produce a basic pH in a neutral solution while L-carbons will produce an acidic pH. Electrokinetic studies have determined

that H-carbons exhibit a positive zeta potential while L-carbons have a negative potential. The negative potential of L-carbons is thought to occur due to the presence of acidic functional groups on the carbon surface such as phenol, n-lactone, and f-lactone. Kolthoff (1963) discovered that hydrogen peroxide is released into solution from which acid is adsorbed. Based on this discovery, Garten and Weiss (1965) proposed the existence of chromene (benzpyran) groups on the surface of H-carbons. The acid reaction with the chromene group will form a carbonium ion which will hydrolyze in water to form a chromenol group, a weakly basic group (Snoeyink and Weber, 1967). Thus, the presence of the chromene groups on the surface of H-carbons is responsible for the acid-adsorbing characteristics.

Activation temperatures and oxidizing conditions not only affect the type of functional groups found on the surface of the activated carbon, but also affect the pore volume distribution as well as pore surface area, two important factors that may determine selectivity as well as capacity for adsorption. Hashimoto, et al. (1979) used three types of coal to study the affects of activation temperature and oxidizing gas on pore volume distribution, pore surface area, and adsorption performance with a surfactant, dodecyl benzene sulfonate (DBS). Chars were used from three sources, Miike coal (MC) from Japan, Victoria coal (VC) from Australia, and coconut shell (CS), and were activated. The

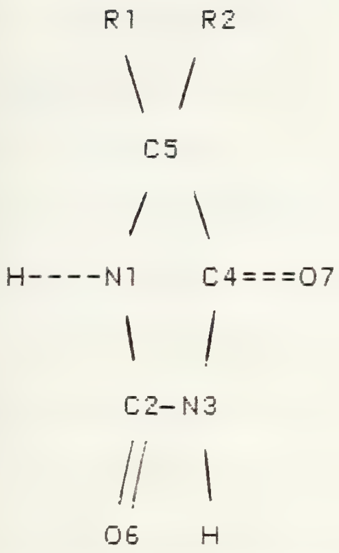
reaction temperatures used for MC were 800°C, 850°C, and 900°C. The other two, VC and CS, were activated at 850°C. Carbon dioxide and steam were the oxidizing gases used in the activation of MC while steam alone was used to activate the others. Three different particle sizes were used for MC (8 x 9.2, 14 x 16, and 42 x 60 Tyler mesh) and one size (14 x 16 mesh) was used for VC and CS. The results of their experiments showed significant differences in the pore volume distributions for the different oxidizing gases and starting materials. MC activated by steam had a typical bimodal distribution (high volume of pores at 6-10 A and at 4-6 x 10^4 A with a constant distribution of intermediate pore sizes), MC activated by carbon dioxide had little micropore volume and a large macropore volume, VC had a gently sloping distribution high in micropore volume to a low in macropore volume, and CS had a large micropore volume and little macropore volume. Both VC and CS were oxidized by steam. The reason proposed for the difference in the pore volume distribution for the MC for CO_2 and steam was that the activation reaction of CO_2 catalyzed by mineral matter on the surface such as iron or nickel would result in the formation of macropores, but could not increase the volume distribution of the micropores. The differences in the pore volume distributions for the other starting materials was determined to be dependent upon the initial pore structures of the starting materials. The highest micropore

volume (pores < 100 A) was determined to occur at burnout levels of 40-60% for MC and VC and at 30% for CS.

The effects of the different starting materials and activation conditions on carbon surface area were studied as well. The order of surface areas determined was CS > VC> MC(steam) > MC(carbon dioxide), respectively. The maximum surface area was obtained at lower burnoff levels generally reaching a maximum at 30-60% burnoff. The pore surface area decreased as the activation termperature increased from 800°C to 850°C to 900C. In comparing the adsorption isotherms for dodecyl benzene sulfornate (DBS) on MC activated by steam with different burnout levels, it was determined that as the burnout level increased, the adsorption capacity increased to a maximum at some burnout level, then decreased. The maximum adsorption capacity was obtained at 50-60% burnout. In studying adsorption columns with the same carbons, the breakthrough time increased as the amount of burnoff increased, and would reach a maximum. From the column studies, it was determined that the breakthrough time for MC at 52% burnoff was 6.5 times greater than the breakthrough time for MC at 22% burnoff, but the pore surface area for the MC at 52% burnoff was only twice as large as the surface area for MC at 22% burnoff. Therefore, it was determined that the activation did not increase the pore surface to such a large extent, but increased the size of the pore radius and thereby, the adsorption capacity of the

pores. The work of Hashimoto et al., clearly indicates that a difference in starting materials and activation temperatures can affect the adsorption characteristics of the final activated carbon. The difference in activation temperatures affects the size of the pore radius and to a lesser extent, the pore surface area. The pore redius is a selective factor, since an adsorbate cannot be adsorbed to any great extent if it cannot readily travel through the carbon pore mouth. The pore or cumulative surface area affects the number of adsorption sites available for adsorption. The greater the cumulative surface area, the more adsorption that can be expected to occur for any given system of adsorbate and solution.

Adsorbates. The adsorbates used were hydantoin (I), 5,5-dimethylhydantoin (II), and 5-ethyl-5-methylhydantoin (III). In the literature, hydantoin is technically listed as 2,4-imidazolidiniedione, has the formula $C_3H_4N_2O_2$, and is typically found in anticonvulsants, heat resistant rubber and insulation, dry resistant inks, light stabilizers for plastics, and tobacco smoke. The molecule is a pentagonal heterocycle as shown below:



I. $R_1 = R_2 = H$

II. $R_1 = R_2 = CH_3$

III. $R_1 = CH_3$, $R_2 = C_2H_5$

The R's represent either hydrogen atoms or alkyl groups. The molecule is nearly planar, and hydantoin crystals are formed by stacking interactions and hydrogen bonds between N(1) and O(6) and between N(3) and O(6). O(7) does not participate in hydrogen bonding (Cassady and Hawkinson, 1981). Zief and Edsall (1937) determined that the ionizing hydrogens arise from the NH groups and not from the CH_2 group. 5,5-Dimethylhydantoin and 5-ethyl-5-methylhydantoin are hydantoin analogs with alkyl groups bonded to C(5).

Hydantoins and its alkyl derivatives are also found in coal gasification wastewater using lignite as a starting material. Olson, et al., (1983) using gas chromatogaphy/mass spectrometric equipment to analyze wastewater from a slagging fixed bed gasi-

fier using Indian Head lignite for fuel determined the following components to be present:

5,5-dimethylhydantoin
5-methylhydantoin
5-methyl-5-propylhydantoin
5-ethyl-5-methylhydantoin
5-isopropyl-5-methylhydantoin
1,3-dimethyl derivatives

5,5-Dimethylhydantoin was found to be the most dominant component in the wastewater followed by 5-ethyl-5-methylhydantoin. The concentration of hydantoins in the condensate water varied with different operating temperatures and types of coal used as the starting material. The quantity and class of ketones (from which hydantoins are synthesized) in the wastewater varied with the moisture content and ash-free content of the starting coal. The residence time and temperature of the condensate water in the tar/oil/water separator or spray washer may affect the amount and rate of synthesis of the hydantoins from the ketones (Olson,et al., 1983). The hydantoin concentration in coal gasification wastewater is highly dependent upon the operating conditions of the gasifier and subsequent waste treatment processes. Hydantoins must be removed from wastewaters since these polar compounds are not solvent-extracted or readily degraded by chemical or biological oxidation (Willson,et al.1983). The affects of the release of hydantoins into the environment are wholly unknown at the present time, but these compounds are known carcinogens.

Solvent and Solute Interactions. Although surface area, pore diameter, and surface functional groups on the carbon particle are important in determining adsorption capacity, the solvent and solute characteristics and interactions are also important. Quite often, Traube's Rule is followed (Mattson and Mark, 1971). Traube's Rule specifies that polar solutes are preferentially adsorbed by polar adsorbents from non-polar solutions, and non-polar solutes are preferentially adsorbed by non-polar adsorbents from polar solution. The affinity of the adsorbent for the solvent used is also critical. Should the adsorbent have a high affinity for the solvent, more adsorption energy is required for the solute to physically displace the solvent molecules from the adsorbent surface. An example of where this relationship is important is the adsorption of dimethylformamide (DMF) on Aerosil silica (Lipatov and Sergeeva, 1974). The affinity between DMF and Aerosil silica is high. The addition of DMF to a solution of a given adsorbate markedly reduces the adsorption of that adsorbate. This is probably due to the strong adsorption of polar DMF on silica competing with the other adsorbate for adsorption sites. Water would also probably compete with adsorbate for adsorption sites due to its polarity. Also, should the solvent have a high affinity for the solute, the adsorption of the solute from solution would be reduced. A higher Gibb's free energy would be required to move the solute from bulk solution to the surface,

and the higher the free energy of the reaction, the less the reaction will occur. Koral, et al. (1965) studied the adsorption of polyvinyl acetate on carbon, and determined that adsorption capacities decreased in order from solutions of methanol, toluene, benzene, acetone, trichloroethylene, 1,2-dichloroethane, and chloroform. In chloroform, where the solubility of polyvinyl acetate is the greatest, no adsorption was observed (Lipatov, 1974).

Water as a solvent, may also hydrate the solute molecules making them larger than their actual size. The hydrated molecules may be large enough to be excluded from the mouth of the carbon pores, and thus, water may indirectly act as a selective agent for adsorption.

The interactions between the individual solute molecules in solution may also affect the adsorption process. Tamamushi (1983) found while working with surfactants and polar adsorbents, such as alumina, polar groups of surfactant molecules would be attracted to adsorption sites on the surface by electrostatic attraction forming oriented monomolecular layers. Bimolecular layers would then be formed by Van der Waals attractive forces between the non-polar chains of surfactant molecules (Tamamushi, 1983). Therefore, the adsorption of surfactant from solution was increased due to interactions between adsorbed molecules and other surfactant molecules in bulk solution.

The solution pH in concert with the solute dissociation constant determines the solute species, either ionic or neutral, that will predominantly occur. With non-polar carbon, neutral species tend to be more readily adsorbed than polar species. Solution pH may also affect the polarity of the surface functional groups on the carbon surface. A charged carbon surface caused by the dissociation of surface functional groups may electrostatically attract or repel the solute in solution which would either enhance or diminish the adsorption capacity. Routinely, the pH used for adsorption in wastewater treatment is the pH of the influent wastewater. Perrich (1981) noted, however, that in the case of organic acids and bases, it may be beneficial to adjust the pH for a less soluble, more adsorbable species to occur in solution. The reduced carbon dosages required and improved economics frequently offset the additional costs of pH adjustment in these applications (Perrich, 1981).

Temperature variations of the solution alter the solubility of the solute, increase or decrease the mobility of the solute and solvent molecules (decreases the fluid viscosity assuming delta T > 0) and influence the competition between the solute and solvent molecules for adsorption sites. Usually, increases in temperature decrease the amount of adsorption that will occur. However, this is not always the case. On carbon, the adsorption of polymethyl methacrylate decreases with increasing temperature,

that of polyvinyl chloride increases, while the adsorption of polystyrene is practically temperature independent (Lipatov, 1974). This difference is attributed to the diferences in solute solubility that occurs in the interactions between solute and solvent with temperature variations. In adsorption studies, temperatures are maintained with a minimum of variation to preclude differences in adsorption capacity due to changes in solute solubility with temperature.

The mixing speed of the solution also affects the kinetics of the adsorption process. With quiescent adsorption, the adsorbent particles will have a boundary layer of solution around the particle which must be traversed by the solute prior to adsorption. This process may be and often is rate limiting to the process and will increase the time required for physical adsorption to occur on all available adsorption sites. With adequate mixing, the boundary layer around the particles may be sufficiently reduced in thickness to cause migration across the boundary layer not to be rate limiting.

Solutes. The configuration and molecular weight of the solute also plays a role in the adsorption process. The rate of adsorption of smaller molecules is higher than that of larger molecules due to differences in diffusivity. In a multi-solute adsorption study, the smaller molecules will be adsorbed first to

individual and combined interactions. For activated carbon, the adsorbent may come from a variety of starting materials activated at different process temperatures. Either variable may affect the type of surface functional groups, the acid-base character of the carbon, the pore surface area and size distribution, and surface charge which may affect the adsorption capacity and selectivity. The solution variables of temperature, pH, mixing speed, and polarity affect adsorption through physical and chemical interactions with the adsorbent and solute. The variations in solutes of size and configuration, molecular weight, dissociated or neutral species, and interactions between solute molecules in solution and adsorbed phases also affect the amount of solute adsorbed from solution. From the number of variables involved, it's not too surprising that a variety or models exist to describe the adsorption process, and one model that accurately describes one adsorption system may not work at all when applied to a different adsorption system.

Langmuir and Freundlich Adsorption Equations. Two of the oldest and still popular adsorption isotherm equations were those developed by Freundlich and Langmuir (Jain and Snoeyink, 1973). The Langmuir equation is based upon the assumptions of 1) localized adsorption, 2) no interaction between adsorbed molecules, 3) no more than one molecule per adsorption site, 4) all sites have equal adsorption energies, and 5) no migration of adsorbed mole-

be eventually displaced by larger molecules, corresponding to the thermodynamic equilibrium state.

Concerning the configuration of solute molecules, Belfort (1979), in studying the adsorption of organic homologues on activated carbon, determined that rigid spherical molecules (2-methyl-2-propanol or 2-propanol) have less surface area to interact with the carbon surface than a flexible rod-like molecule (1-butanol or 1-propanol). Also, increased branching tends to decrease adsorption capacity. In studying the conversion of aldehydes to ketones by the replacement of a hydrogen by a methyl group, Belfort (1979) determined that adsorptivity increased as follows.

	increased adsorption (g -mole/g)
acetaldehyde/acetone	2.41×10^{-4}
propionaldehyde/methyl ethyl ketone	3.23×10^{-4}
butyraldehyde/methyl propyl ketone	1.44×10^{-4}

Increased adsorptivity was also encountered with the addition of OCH_3 and CH_3 groups to aromatics.

In summary, the adsorption process is affected by many variables involving the adsorbent, solute and solvent and their

cules on the surface plane of the adsorbent. The equation takes the following form for a single adsorbate system:

$$X = X_m bC/(1 + bC) \qquad (1)$$

and may be linerarlized as follows:

$$1/X = 1/X_m + (1/bX_m)(1/C) \qquad (2)$$

where:

X = the amount of solute adsorbed per unit weight of adsorbent,

X_m = maximum value of X that corresponds to monolayer coverage of the adsorbent,

C = equilibrium concentration, and

$b = b_o \exp(-E/RT)$,

b_o = constant containing the entropy term,

E = energy of adsorption,

R = universal gas constant, and

T = absolute temperature.

The Freundlich isotherm equation can be presented by the following equation (Perrich, 1981):

$$X = KC^{1/n} \qquad (3)$$

where:

K and n = constants.

Taking the logarithm of both sides gives:

$$\log X = \log K + (1/n)\log C \qquad (4)$$

On a log-log plot, this gives an equation with a straight line with a slope of 1/n and an intercept K at C = 1. When values of K and n are determined, the resulting equation can be used to predict X values within the range of experimental data. The Freundlich equation's basis in theory includes immobile adsorption and an exponential distribution of adsorption site energies. However, the Freundlich equation may describe portions of adsorption isotherms of organics on activated carbon in dilute aqueous solutions.

Many other adsorption models and equations exist which include the Gibbs adsorption isotherm, the Brunaer, Emmet, and Teller (BET) model, the capillary condensation model, the Polanyi adsorption potential model, the solvophobic adsorption theory, and the net adsorption energy theory. However, no existing adsorption theory takes into account the aqueous solvent competing for adsorption sites or can predict the preferential adsorption of organics on activated carbon without laboratory experiments (Miller, 1980).

3. Scope of Study

The research involved performing a carbon adsorption study on three compounds: 1) hydantoin, 2) 5,5-dimethylhydantoin, and

mination of the amount of solute adsorbed per unit weight of carbon under continuous flow conditions and under competition. The carbon adsorption column using undiluted coal gasification wastewater was utilized to qualitatively determine the effectiveness of carbon in removing hydantoins from the wastewater.

The ultimate purpose of the research was to determine to what extent activated carbon would adsorb the three hydantoin analogs studied, and to determine if activated carbon adsorption is a viable treatment alternative for the coal gasification wastewater.

4. Methods and Materials

The experimental work consisted of obtaining calibration curves for analysis, single solute batch kinetic tests, and single, bisolute, and trisolute isotherm and column studies for each of the three adsorbates, hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin. Also, a column study was performed on undiluted coal gasification wastewater. The materials used and each phase of the experimental work will be considered separately.

Adsorbent. The adsorbent used for all experiments was Calgon Filtrasorb 400, a bituminous based activated carbon (Calgon Corp.). The physical properties of Filtrasorb 400 are reproduced from Rossello (1981) and are set forth in Table 2:

Table 2. Physical Properties of Filtrasorb 400

Total surface area (N_2BET method), m^2/g	1050-1200
Bulk density, lb/ft^3	25
Particle density, wetted in water, g/cc	1.3-1.4
Pore volume, cc/g	0.94

The pore size distribution reproduced from Rossello (1981) is shown in Figure 1. Of the 0.94 cc/g pore volume 0.54 is made up of micropores (<100 A.). The remaining 0.40 cc/g is made up of macropores.

3) 5-ethyl-5-methylhydantoin. The carbon adsorption study consisted of the following:

a) calibration curves for each adsorbate,

b) single solute batch kinetic studies,

c) single solute isotherm studies,

d) bisolute and trisolute isotherm points,

e) single solute column studies, and

f) bisolute and trisolute column studies.

In addition, a column study using undiluted coal gasification wastewater containing predominantly hydantoin compounds was performed.

The calibration curves were performed to enable the determination of solute concentration of any single solute sample using a UV-visible spectrophotometer. The single solute batch kinetic studies were utilized to determine the elapsed time required for solution equilibrium to occur in a solute-carbon adsorption system. The bisolute and trisolute isotherm points determined the adsorption performances of activated carbon for the three solutes during solute competition. The single solute column studies determined the amount of solute adsorbed per unit weight of carbon adsorbent under continuous flow conditions, and provided insight into the relative rates of adsorption of the three solutes. The bisolute and trisolute columns allowed deter-

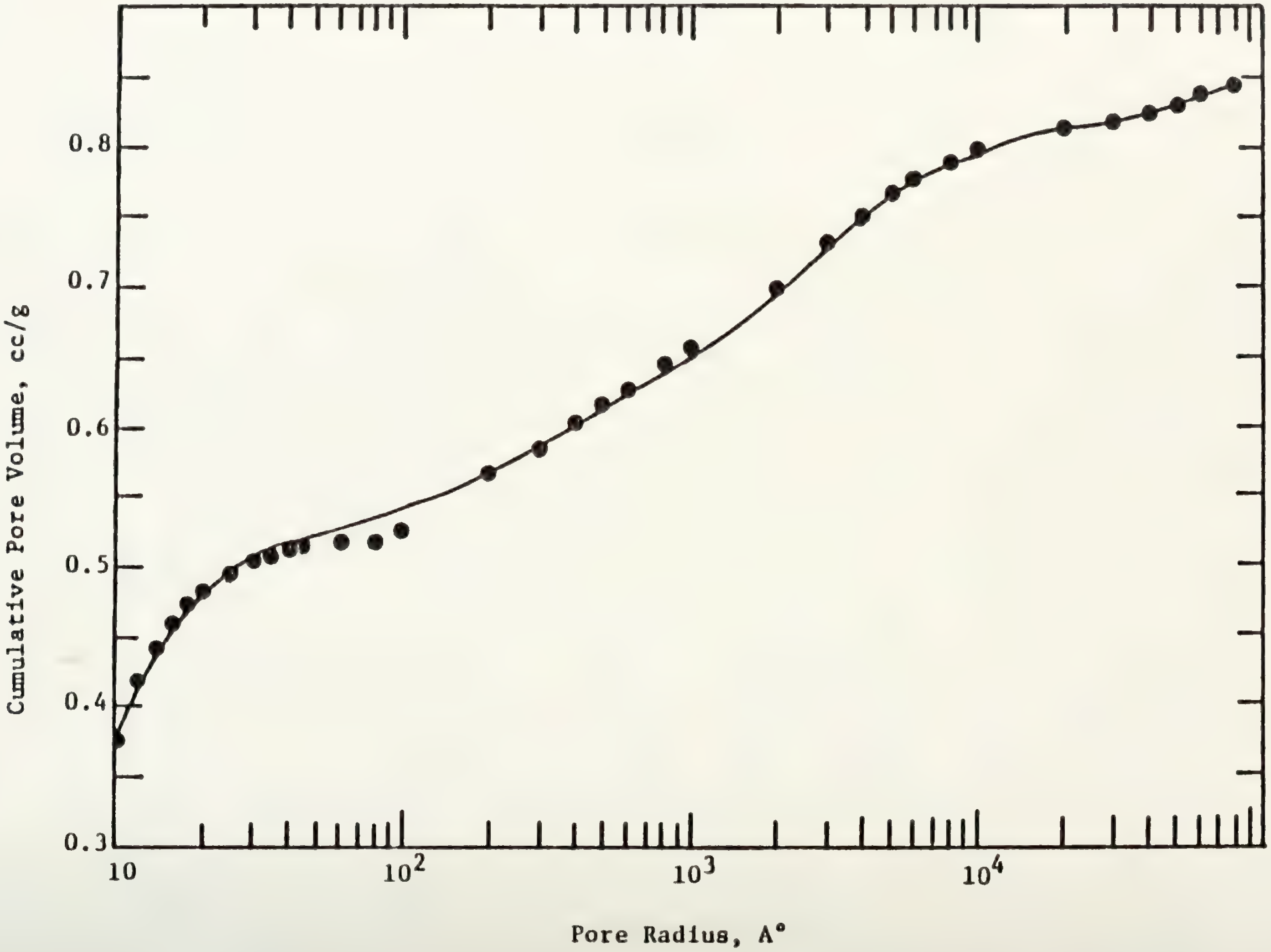


Figure 1. Pore Size Distribution of Bituminous Base, Filtrasorb 400 Activated Carbon

The carbon used in the experimental work was mechanically ground to obtain a size distribuion of U.S. standard sieve 60 x 80, washed to remove fines, and dried at 103°C for 3 days to remove moisture. The carbon was then stored in a covered acid washed bottle prior to use.

Adsorbate. The adsorbates used were hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin. The hydantoin and 5,5-dimethylhydantoin were products of Aldrich Chemical Co. The 5-ethyl-5-methylhydantoin was provided by Dr. W.H. Cross.

The characteristics of the adsorbates are given in Table 3:

Table 3. Characteristics of Adsorbates

hydantoin	
melting point	220°C
molecular wt.	100.08
pKa	9.12
5,5-dimethylhydantoin	
melting point	178°C
molecular wt.	128.14
pKa	9.20
5-ethyl-5-methylhydantoin	
melting point	180°C
molecular wt.	142.17
pKa	9.20

Calibration Curves. Standards were prepared by measuring quantities of solid adsorbate directly into weighed 50 ml or 100 ml volumetric flasks. A Mettler annalytical balance (Mettler Instrument Co., Model H542) was used for all weight measurements. After weighing, the solid adsorbate was dissolved in distilled, deionized water to obtain a solution of known concentration. Standards were prepared in concentrations ranging from 200 mg/l to 0.5 mg/l for each adsorbate.

A Beckman Model 26 UV-visible spectrophotometer (Beckman Instruments Inc., Irvine, Ca.) was used for absorption measurements. A scan of absorbance vs. wavelength was made for each adsorbate. Hydantoin and 5-ethyl-5-methylhydantoin each had a maximum absorbance at a wavelength of 193 nm. 5,5-Dimethylhydantoin had a maximum absorbance at 198 nm.. Absorbance responses were measured for each standard three times with responses in the range of + or -0.005 absorbance units (+ or - 1-2%). The response data was plotted as absorbance vs. concentration (mg/l) to obtain calibration curves. The calibration curves are shown in Figures 2,3, and 4.Thereafter, solutions to be measured using the spectrophotometer were diluted,when required, for the absorbance response to fall within the linear portion of the calibration curve. Generally, the calibration curve began to be non-linear at concentrations greater than 50 mg/l.

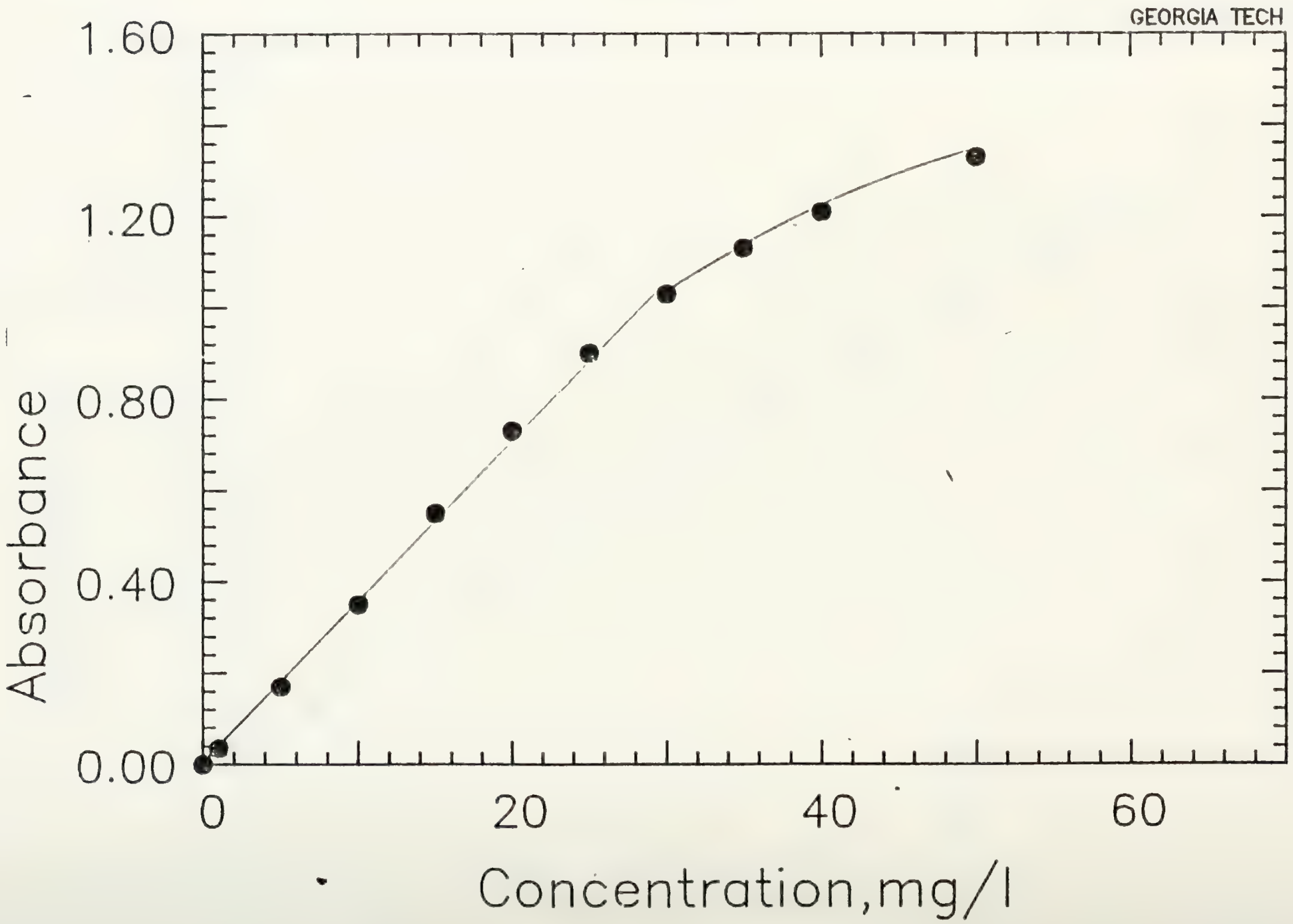


Figure 2. Calibration Curve for Hydantoin

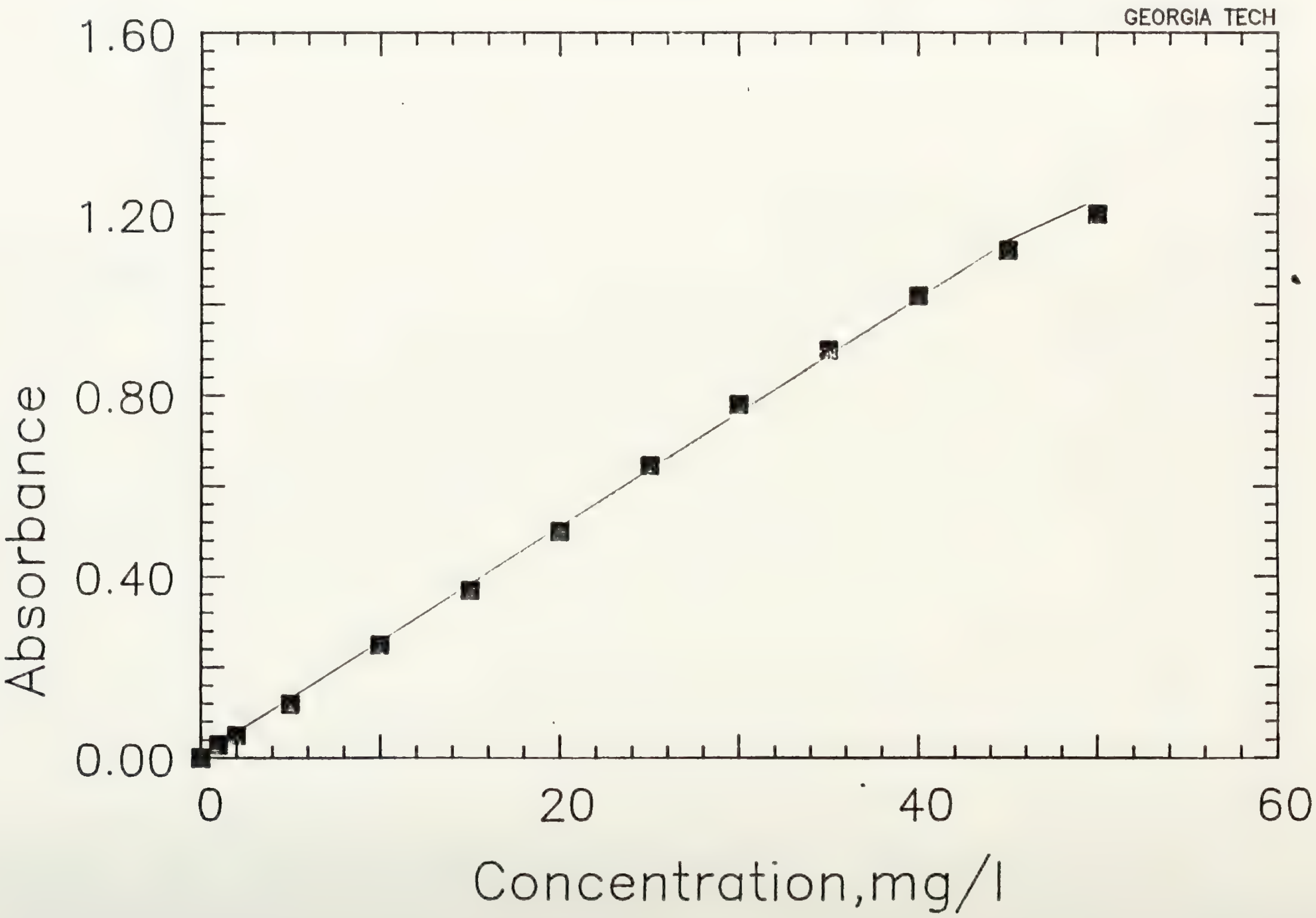


Figure 3. Calibration Curve for 5,5-Dimethylhydantoin

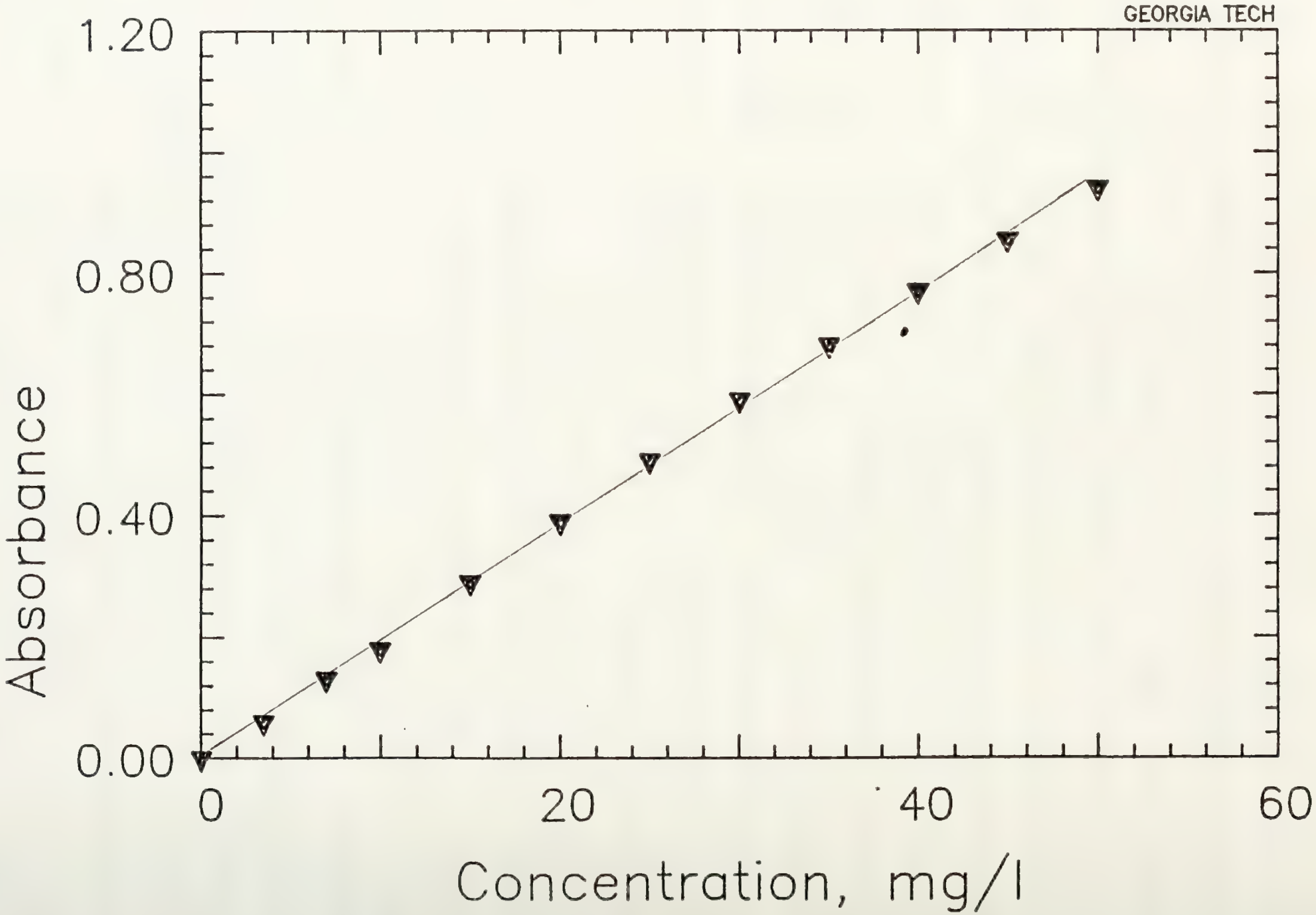


Figure 4. Calibration Curve for 5-Ethyl-5-methylhydantoin

Batch Kinetic Tests. Batch kinetic tests were performed to determine the required time for the adsorbate to reach an equilibrium concentration with the activated carbon. A 4-liter beaker was used as a reaction vessel. Adsorbate was added to the vessel, 4 liters of deionized water added, and mixed for 1 hour to allow all adsorbate to dissolve and for the solution temperature to equilbriate to room temperature. The stirrer used was a Fisher laboratory stirrer (Fisher Scientific Co.) with a three-bladed Nalgene stir rod. The impeller speed was approximately 800 rpm as measured by a Cole Parmer Phototach (Cole Parmer Digital Phototach, Model 1891-M, Chicago, Ill.). Once the adsorbate was dissolved, an initial 5 ml sample was removed, diluted, and analyzed photometrically. This concentration value was used as the initial concentration. Three (3) grams of carbon were added to the vessel and 10 ml samples were taken at intervals of 5, 10, 20, 30, 60, 180 minutes, 5 hours, 24 hours, 30 hours, 48 hours, and 120 hours. Before sampling, the mixing was stopped and carbon particles were allowed to settle.. The sample was then placed in a centrifuge tube, centrifuged at approximately 3000 rpm for 1 minute to remove interferences from any residual carbon fines. An aliquot of the supernatant was removed by pipette, and any additional solution remaining in the centrifuge tube was returned to the reactor vessel. The samples were analyzed to determine the

solute concentration. The results of the batch kinetic tests were plotted by concentration (mg/l) vs. time (hours).

Isotherms. Isotherms are used to calculate the amount of adsorption per unit weight of adsorbent for various equilibrium concentrations. From this data, the amount of carbon required to obtain a given equilibrium concentration in the solution can be determined. Isotherms are generally performed with a series of bottles with varying solute concentrations with fixed amounts of carbon or varying amounts of activated carbon with a fixed concentration of solute. The bottles are placed in a shaker and allowed to come to equilibrium, and the final concentration of solute is then measured.

The single solute isotherms were performed by preparing a 2000 mg/l stock solution of the adsorbate. The batch reactors were 125 ml square glass bottles with screw caps. All glassware was acid cleaned with a 10% nitric acid solution and rinsed with distilled water. Aliquots of the stock solution were diluted to 100 ml concentrations of 300, 280, 260, 240, 200, 190, 180, 160, 140, 120, 100, 90, 80, 70, 60, and 50 mg/l. For greater dilutions, a 40 mg/L stock solution was prepared and diluted to give solutions containing 40, 20, 10, 5, and 2 mg/L. The initial concentration of adsorbate in solution was measured spectrophotometrically. The amount of solution used in sampling was recorded and was accounted for in all calculations.

After the initial concentration had been measured , 125 mg of carbon was added to each bottle. The bottles were tightly capped and then, placed on a shaker table (New Brunswick Scientific Company, Model VS, Ser 861114, New Brunswick, NJ). The shaker rotated at approximately 500 rpm as measured by a phototach. The bottles were placed in a wooden box attached to the shaker table at an angle of 15^{0} with respect to horizontal to provide additional mixing action. Mixing time used was 24 hours to ensure that solution equilibrium had been attained. To ensure equilibrium, sample bottles were shaken an additional three days with no change in solute concentration. After 24 hours, the equilibrium concentration of solute was determined. The calibration was checked at the beginning, midpoint, and end of each series of tests. Absorbance readings were accurate to + or - 0.005 absorbance units. The difference between the initial concentration and the final concentration of solution represented the amount of solute adsorbed. Knowing the amount of carbon added to the bottle and the volume of the solution, the amount of adsorbate per unit weight of carbon (X/m) could be determined where X is the amount of adsorbate adsorbed and m is the weight of carbon used. The results were plotted on a log-log plot of X/m as ordinate and equilibrium concentration, C_{eq}, as abscissa.

A different approach was used for the bisolute and trisolute isotherms. The equilibrium concentration of the multisolute isotherms could not be determined by the spectrophotometer, since the wavelengths at which the adsorbate concentrations were measured, 193 nm and 198 nm, were too close to prevent absorbance interference between the various solutes. In these cases, a Beckman Total Organic Carbon (TOC) Analyzer (Model 915, Beckman Instruments, Inc., Fullerton, Ca.) to measure total organic carbon and a Perkins-Elmer Sigma I gas chromatograph (GC) (The Perkin Elmer Corp., Norwalk, Conn.) using a PE Sigma 10 Data System was used to measure 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin. The difference between the values for TOC and the GC values for 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin would yield the concentration of hydantoin present. The gas chromatograph was operated isothermal at 225°C using nitrogen as a carrier gas with a flow rate of 40 ml/min. Flame ionization was used. The GC column used was 6' x 1/4" OD, 2 mm ID, packed with 3% AT-1000 on 100/120 mesh Chromosorb W-HP (Alltech Assoc., Deerfield, Ill.) Twenty-five (25) microliter samples were used for the TOC analysis by means of an automatic syringe. The sample volume used for the gas chromatographic analysis was one (1) microliter.. The minimum error that can be expected by using gas chromatographic analysis is + or - 10% (Cross, 1984).

Due to the methods required for analysis of the bisolute and trisolute isotherm points, 100 ml of stock solution was poured into each of two bottles, one used for the control and one bottle used for the isotherm point. The solution was made up of a mixture of equal quantities of hydantoin and 5,5-dimethylhydantoin, hydantoin and 5-ethyl-5-methylhydantoin, or 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin. The trisolute mixture was a mixture of equal quantities of each of the three compounds. For the bisolute mixtures, 125 mg of carbon was added to the isotherm point, no carbon was added to the control, and both bottles were shaken for 24 hours. After equilibrium was reached, the solute concentrations were determined. Individual X/m values for each solute were calculated. For the trisolute mixture, the same experimental procedure was followed with the exception of the amount of carbon added to the isotherm bottle. For the trisolute bottle, 250 mg of carbon was added to ensure that measurable adsorption of each solute would occur.

Adsorption Columns. Adsorption column studies were used to evaluate the activated carbon under continuous flow conditions which more closely approximate the field applications. For the single, bisolute, and trisolute columns, pyrex glass columns 12 inches long and 7/16" inside diameter with 1" end fittings were used.The columns were used in a downflow mode. A 5 gallon carboy elevated above the column served as a solute reservoir. The

solute flow was controlled using a 125 ml/minute capacity FMI pump (Fluid Metering Inc., Model RPG 150, Oyster Bay, N.Y.). 3/8" Tygon tubing connected the solute reservoir, laboratory pump, column, and drained to a lab sink. The column was packed by filling with washed Ottawa sand of 20 x 30 mesh size at the top of the open column until the column was filled to approximately 4 diameters into the 7/16" diameter portion. Then, 3.25 grams of 60 x 80 carbon were added to the column.. The average length of the carbon column was 8.25 cm. Then, the remainder of the column was packed with clean Ottawa sand. All operations were carried out in a submerged fashion so as not to entrain any air bubbles The Ottawa sand portion used as packing was at least 10 diameters long on each side of the carbon column to ensure that a uniform mass fluid front passed through the carbon column. Deionized water at pH 5.6 was pumped through the column until the pH of the effluent remained constant and the absorbance of the effluent as measured by the spectrophotometer was within + or - 0.005 absorbance units of zero. A 5 gallon reservoir of the single, bisolute, or trisolute solution with pH adjusted to 5.6 (with 0.15 N NaOH) was connected to the column. The flow rate used was 20 ml/min which equates to approximately 20.3 ml/cm^2 (5 gpm/ft^2). The average flow rate used in commercial applications is from 8.1-40.6 ml/cm^2 (2-10 gpm/ft^2). A sample from the reservoir was analyzed for the initial concentration both at the beginning and

end of the column run. The solute solution was then passed through the carbon column with samples taken at 15 minute intervals. Typically, samples were continually taken until 1.5 to 2 hours after total exhaustion of the carbon had occurred. Total carbon exhaustion was determined when column effluent samples had the same solute concentration as the column influent.

The single solute solutions were prepared at a concentration of 50 mg/L of each adsorbate. The bisolute solution contained 50 mg/l of both hydantoin/5,5-dimethylhydantoin, hydantoin/5-ethyl-5-methylhydantoin, or 5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin. The trisolute solution contained 50 mg/l of each solute. The single solute samples were analyzed spectrophotometrically, while the bisolute and trisolute samples were analyzed utilizing TOC and gas chromatography.

The coal gasification wastewater adsorption column was a straight 1" x 12" pyrex glass column packed with 20 x 30 Ottawa sand and 30 g of 60 x 80 activated carbon. The flow rate utilized was 100 ml/min which equates to 5 gpm/ft^2. Samples were taken at 5 minute intervals and were taken continuously after carbon exhaustion had occurred. Two different chromatograph columns were used, AT-1000 for alkyl hydantoins and SP-1000 for phenol and cresols. The phenol-cresol GC column was a 6' x 1/4" OD (2 mm ID) glass column packed with 0.1% SP-1000 on 80/100 mesh CarbopakC (Supela, Bellefonte, Pa.). The GC program was isothermal at

195°C. Nitrogen was used as the carrier gas with a flow rate of 20 ml/min, and a FID detector was used. One microliter samples were used for GC analysis while 25 microliter samples were used for the TOC analysis. Specific solute concentrations were determined by comparison with internal standards.

pH Control. No phosphate buffer system was used to control pH in this experiment. The pKa of the solutes are between 9.1 and 9.2 meaning that at that pH, half of the solute is in the ionic form and half is in the neutral form. At neutral pH and below, the system is essentially cationic in nature. Most experiments with single solutes, bisolutes and trisolutes were conducted at pH's significantly less than 7.0, so that the ionic character of the system remained essentially constant. However, to evaluate the effect of pH on adsorption, several isotherm data points at pH 4, 7, and 9 were obtained for the extreme limits, high and low, and midpoint of the single solute isotherm studies. The pH of the solution during the isotherm tests was maintained at the values of 4, 7, or 9 by use of 0.05 N NaOH and 0.05 N and 0.15 N HCL as appropriate. For pH adjustment, care was taken to use 0.25 ml or less of NaOH or HCL to ensure volume errors would be minimal. For the first three hours, pH was checked hourly and adjusted as necessary. Results of the experiment demonstrated that at pH 4 and 7, the X/m values remained constant with little or no change from the original isotherm points. At pH 9, the X/m

values obtained were consistently much lower than the original isotherm curve. The particular pH of 5.6 was used because two single solute column studies, hydantoin and 5,5-dimethylhydantoin, with no pH control, consistently had an effluent pH of 5.6. In order to maintain the pH constant for all column studies, the pH was adjusted to match that of the first two studies. The important consideration is to maintain the pH value of the solution substantially below the pKa value of the solute to ensure that the ionic character of the solute remained constant. In this case, the solute was essentially in the form of the cationic species.

In the column study with the coal gasification wastewater, the wastewater was used without pH adjustment. The pH of the wastewater was measured at 8.76.

5. Results and Discussion.

Batch Kinetic Tests. The results of the single solute batch kinetics tests are shown in Figures 5, 6, and 7. The initial conditions are shown in Table 4.

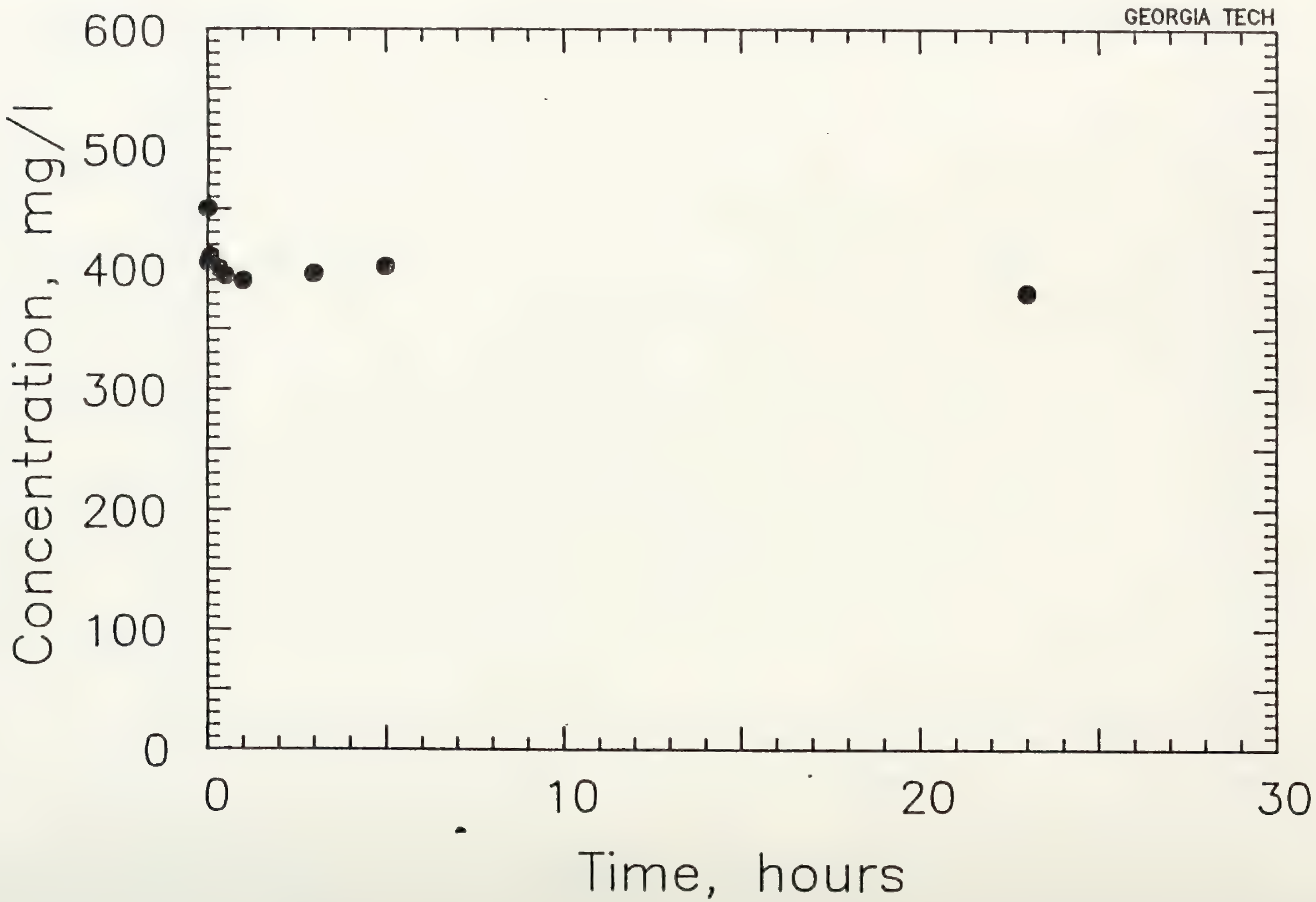


Figure 5. Batch Kinetic Curve for Hydantoin

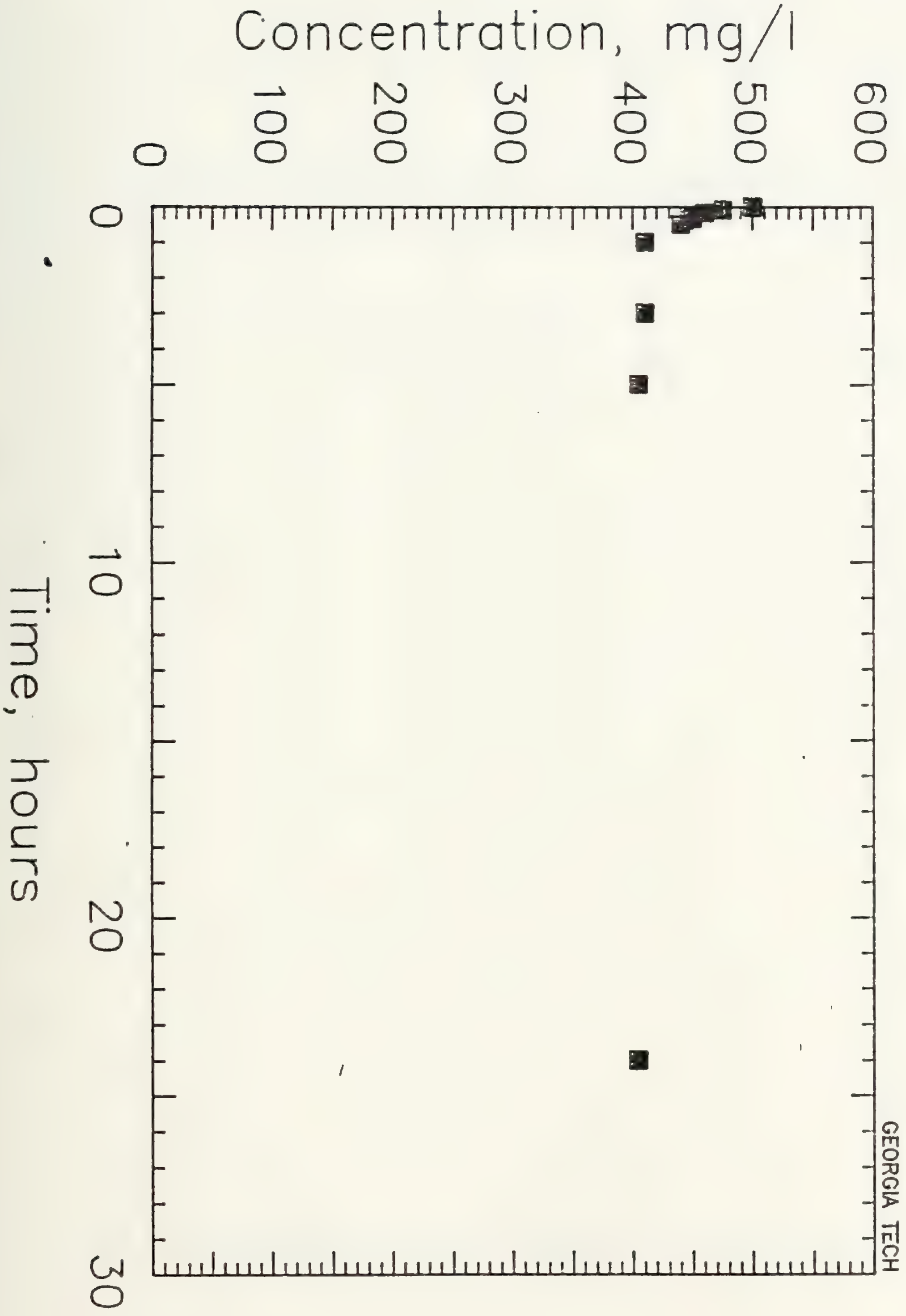


Figure 6. Batch Kinetic Curve for 5,5-Dimethylhydantoin

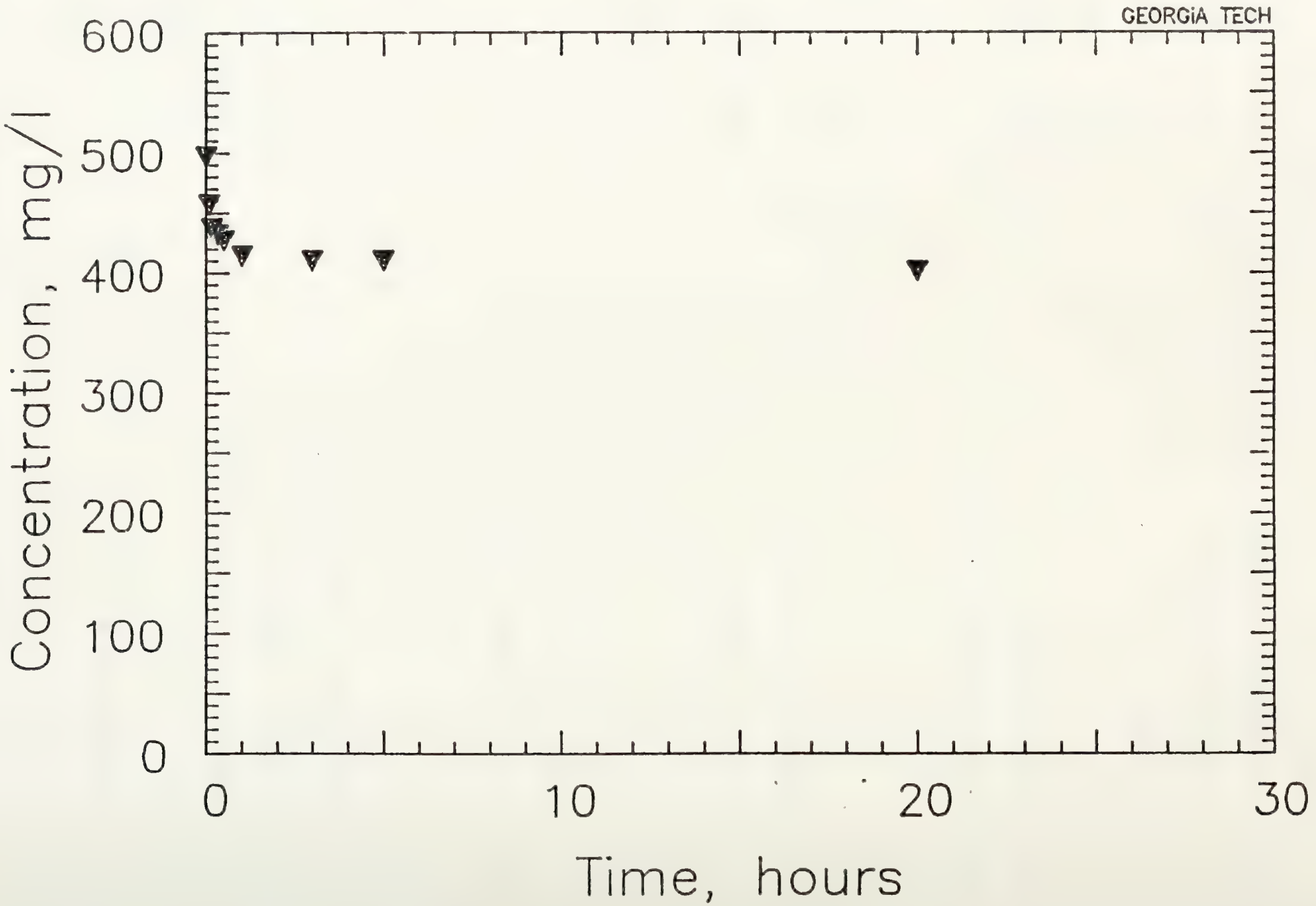


Figure 7. Batch Kinetic Curve for 5-Ethyl-5-methylhydantoin

Table 4. Initial Conditions - Batch Kinetic Tests

hydantoin	
temperature	24° C
C_o	450 mg/L
carbon	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2
5,5-dimethylhydantoin	
temperature	24° C
C_o	500 mg/L
carbon	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2
5-ethyl-5-methylhydantoin	
temperature	25° C
C_o	500 mg/L
carbon	0.75 g/L
stirrer speed	800 rpm
adsorbate volume	4.0 L
pH	approx. 5.2

The batch kinetic study for hydantoin showed a C_o value of 450 mg/l which decreased to 395 mg/l, the equilibrium concentration, in a 1.5 hour time span. In fact, 85% of the adsorption by the activated carbon occurred in the first 20 minutes of the experiment. The same basic sequence occurred for the other two solutes. The batch kinetic tests for 5,5-dimethylhydantoin with a C_o of 500 mg/l reach equilibrium concentration after 3 hours, as did the 5-ethyl-5-methylhydantoin with the same initial concentration. Most of the adsorption of both solutes also occurred in the first 20 minutes of the test.

From the batch kinetic test results, the adsorption of the hydantoins were very rapid. Equilibrium was definitely reached after 3 hours for each compound, and therefore, three hours would be the minimum elapsed time required to ensure that equilibrium concentration is reached. The temperature at which the tests were performed was 24-25°C.

Isotherm Tests. The results of the isotherm tests are shown in Figures 8, 9, and 10.The initial conditions are shown in Table 5.

Table 5. Initial Conditions - Isotherm Tests.

Single solute	
temperature	28° C

C_o	various
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 ml
pH	approx. 5.2

Bisolute

temperature	28° C
C_o	50 mg/L each
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 ml
pH	approx. 5.2

Trisolute

temperature	28° C
C_o	50 mg/L each
carbon	2.5 g/L
shaker speed	500 rpm
adsorbate volume	100 ml
pH	approx. 5.2

The isotherms for hydantoin and 5,5-dimethylhydantoin were very similar with the only difference being a slight increase in

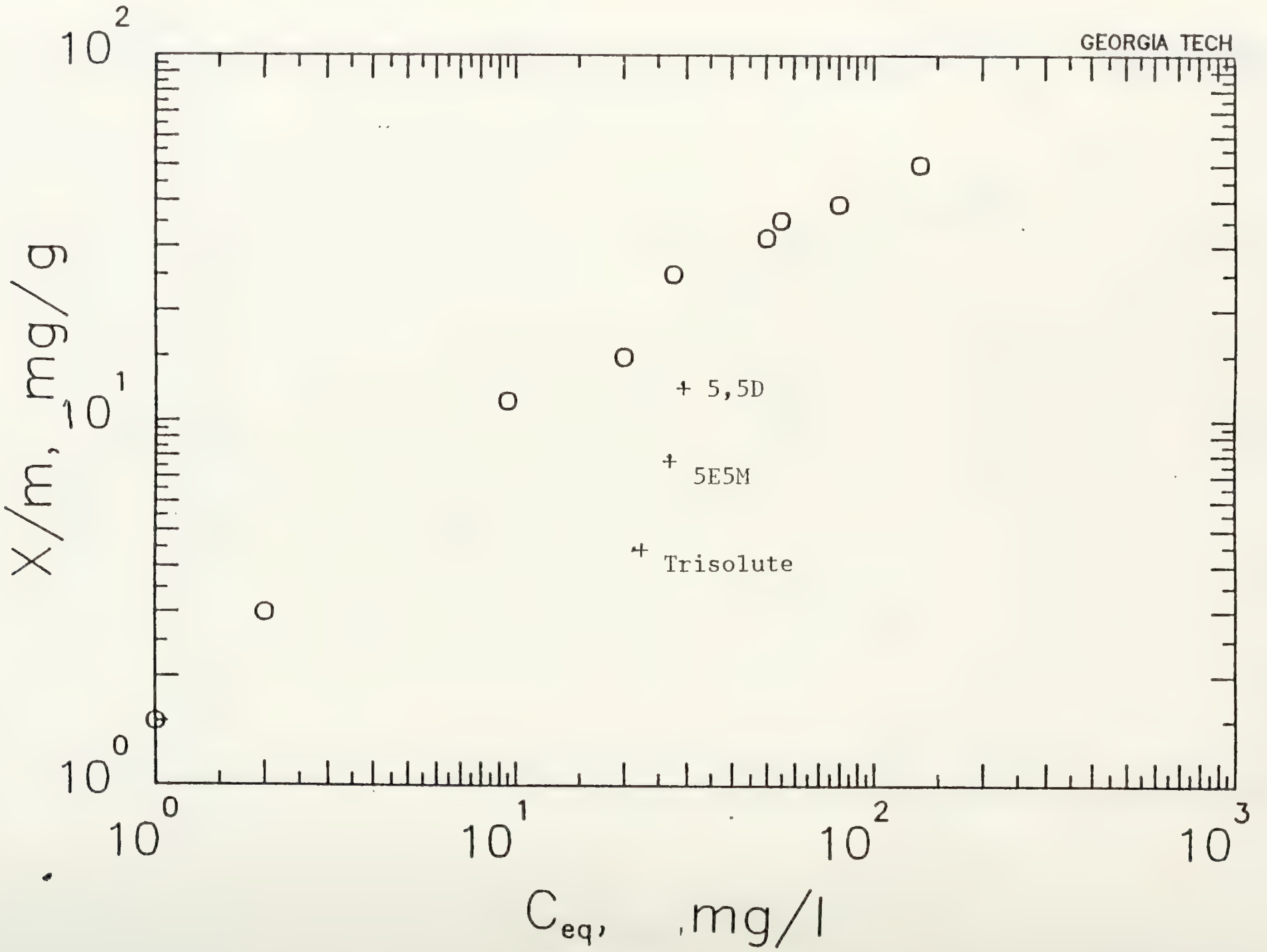


Figure 8. Adsorption Isotherm for Hydantoin

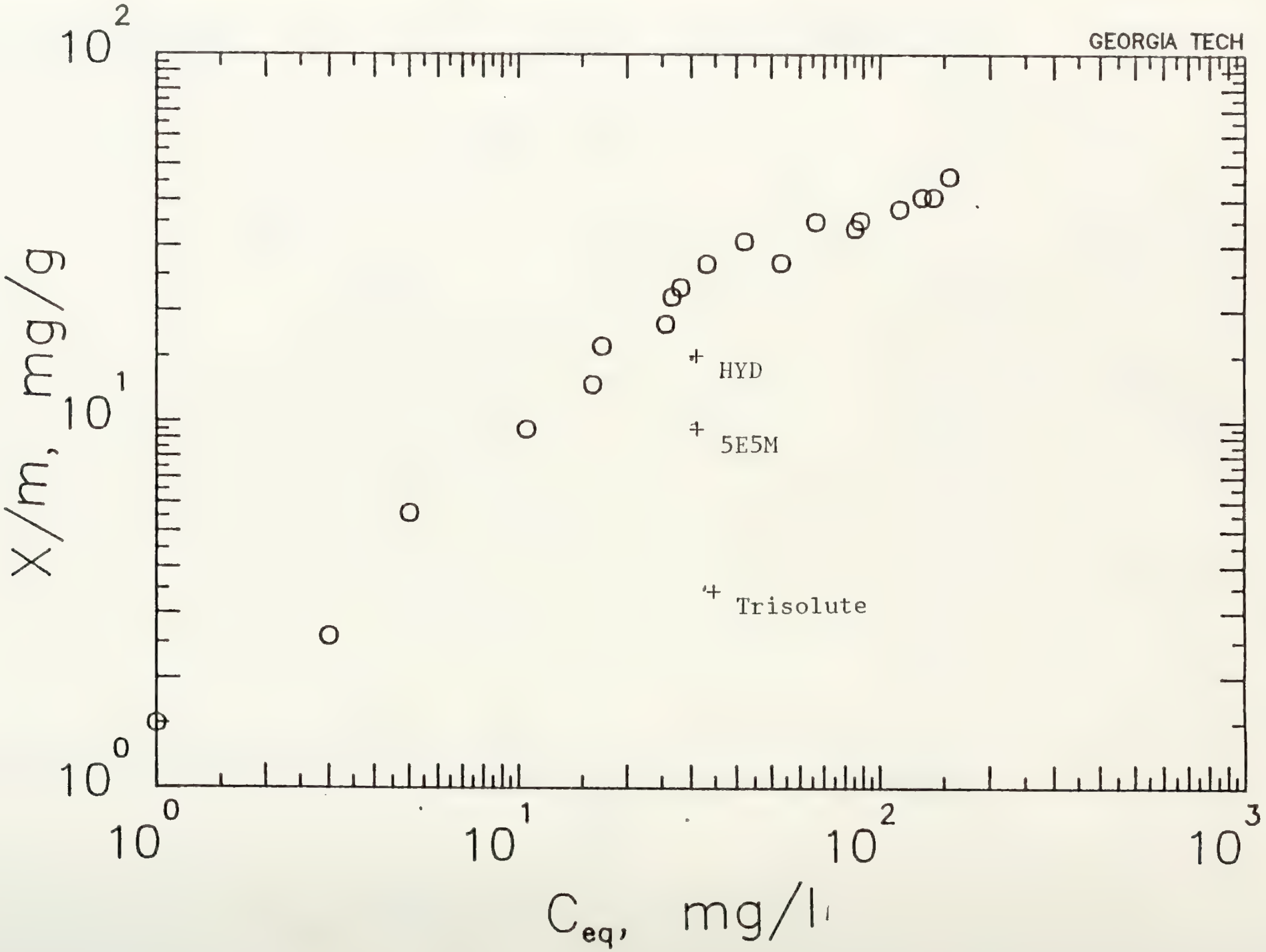


Figure 9. Adsorption for 5,5-Dimethylhydantoin

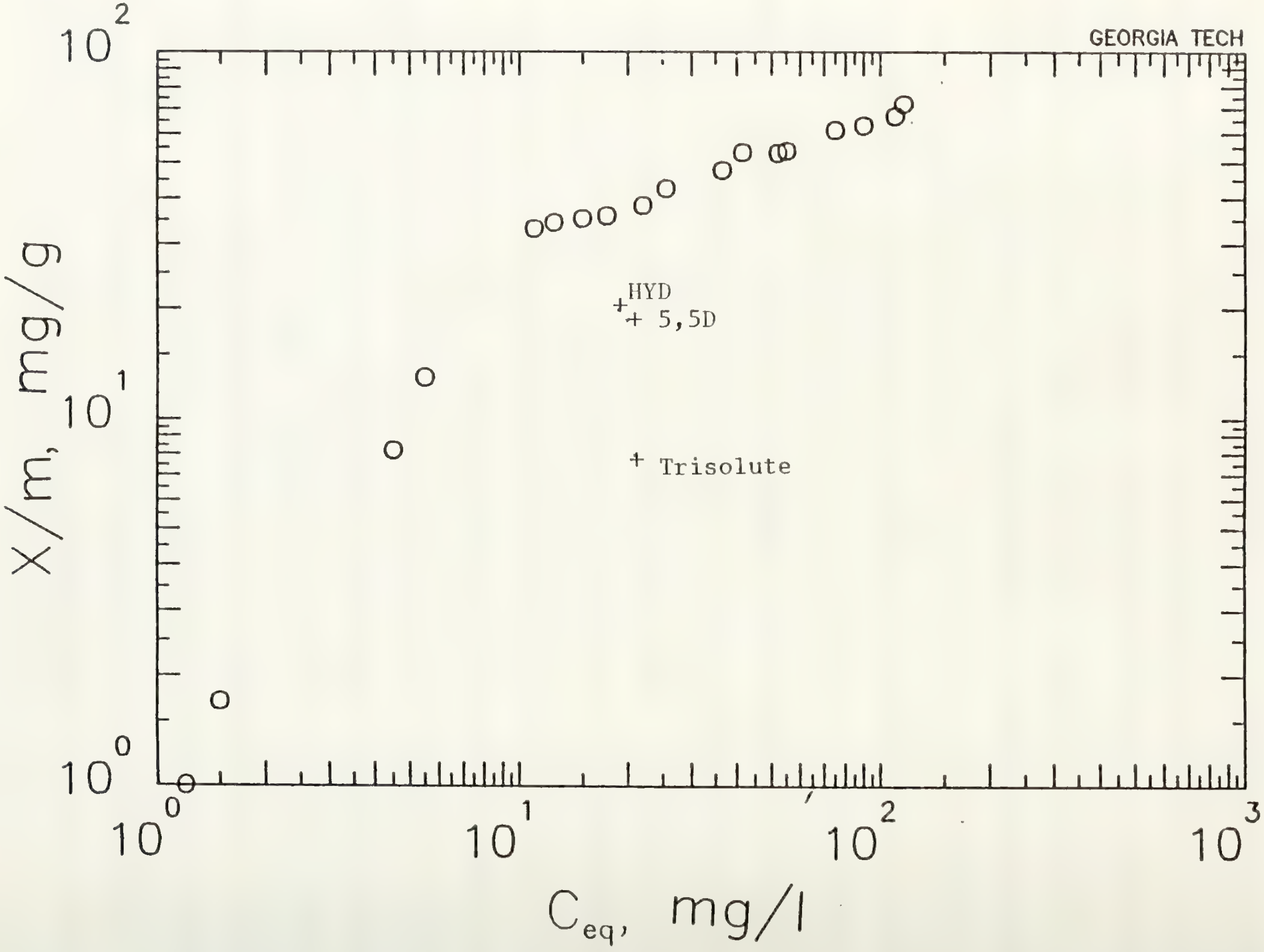


Figure 10. Adsorption Isotherm for 5-Ethyl-5-methylhydantoin

curvature for the 5,5-dimethylhydantoin isotherm over the hydantoin with equilibrium concentrations in excess of 10 mg/l. The X/m values for a given equilibrium concentration were also very similar. The isotherm for 5-ethyl-5-methylhydantoin was much different from the other two solutes. Overall, there was a higher X/m value for any given equilibrium concentration indicating an adsorption preference for 5-ethyl-5-methylhydantoin over the other single solutes. In examining all three curves as a whole, there appears to be a systematic transition in curvature in concentrations in excess of 10 mg/l from hydantoin to 5-ethyl-5-methylhydantoin. Also shown are the results of the bisolute and trisolute isotherm points. Each point represents the X/m and equilibrium concentration found for a given solute in competition with the labelled solute. For instance, in Figure 8, which is the isotherm for hydantoin, the point labelled 5,5 D represents the X/m value found for hydantoin in the bisolute hydantoin/-5,5-dimethylhydantoin isotherm point. The point labelled trisolute represents the X/m value for hydantoin in the trisolute isotherm point. As can be expected, competition tends to reduce the amount of adsorbate adsorbed for a given equilibrium concentration. The relative affinity for the various solutes is also indicated by the fact that less hydantoin was adsorbed when in competition with 5-ethyl-5-methylhydantoin than when in competition with 5,5-dimethylhydantoin. When in competition with two

different solutes, the amount adsorbed is even less. Since there are only a finite number of adsorption sites available, is was reasonable to assume that the increased competition between solutes in the trisolute isotherm point caused less of the individual solutes to be adsorbed than would be the case for the single or bisolute isotherm point.

In comparing each of the bisolute isotherm points, it appears that the relative affinity of activated carbon is in the order of hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin.

The curvature found in the adsorption isotherms represents a departure from the strict Freundlich equation at equilibrium concentrations over approximately 10 mg/l. Therefore, some of the assumptions on which the Freundlich equation are based are invalid for the case in hand. Such assumptions were: 1) exponential distribution of adsorption energies, 2) one adsorbate molecule per adsorption site, 3) no surface transmigration of solute molecules, and 4) monolayer adsorption. The three assumptions may or may not be valid, but it is probable that monolayer adsorption was still occurring at the highest equilibrium concentration tested.

pH Tests. The results of the high, medium, and low isotherm points with pH adjusted to values of 4, 7, and 9 are shown in

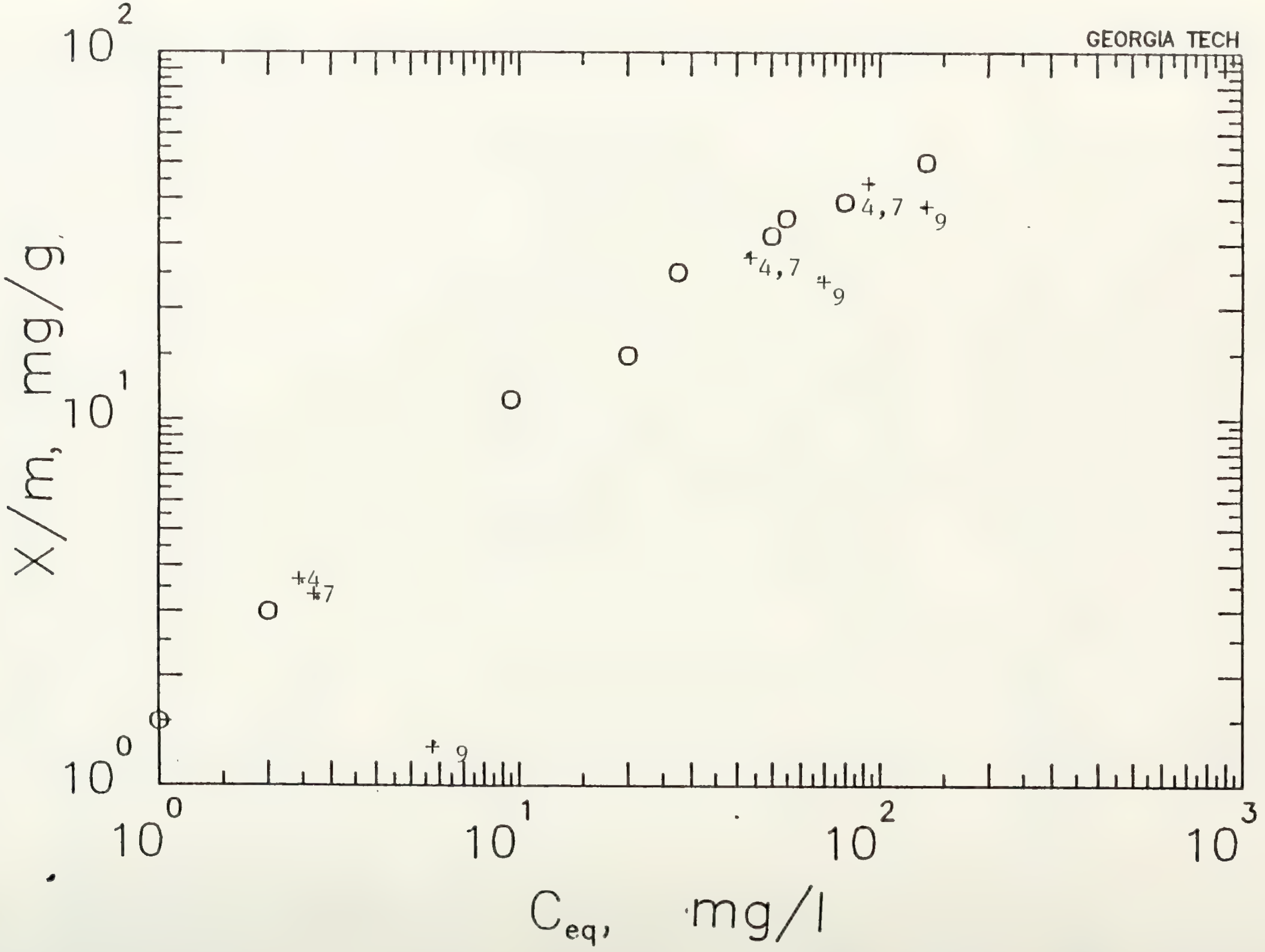


Figure 11. pH Test for Hydantoin

Figures 11, 12, and 13. The initial conditions for each of the three solutes are shown in Table 6.

Table 6. Initial Conditions - pH Tests

temperature	28^{o} C
C_o	50 mg/L
carbon	1.25 g/L
shaker speed	500 rpm
adsorbate volume	100 ml
pH	4,7,9

The isotherm points with pH adjusted to 4 and 7 provided equal X/m values for all three solutes at the medium and high concentration points. The variation in X/m values at the low isotherm points were small and probably due to experimental error. Of consequence were the X/m values of the isotherm points with the pH adjusted to 9. These points have X/m values significantly lower than the single solute curve and the X/m values at pH 4 and 7. Therefore, less solute is adsorbed at pH 9 than at a pH of 4 or 7.

Column Studies. The initial conditions for the column studies are shown in Table 7.

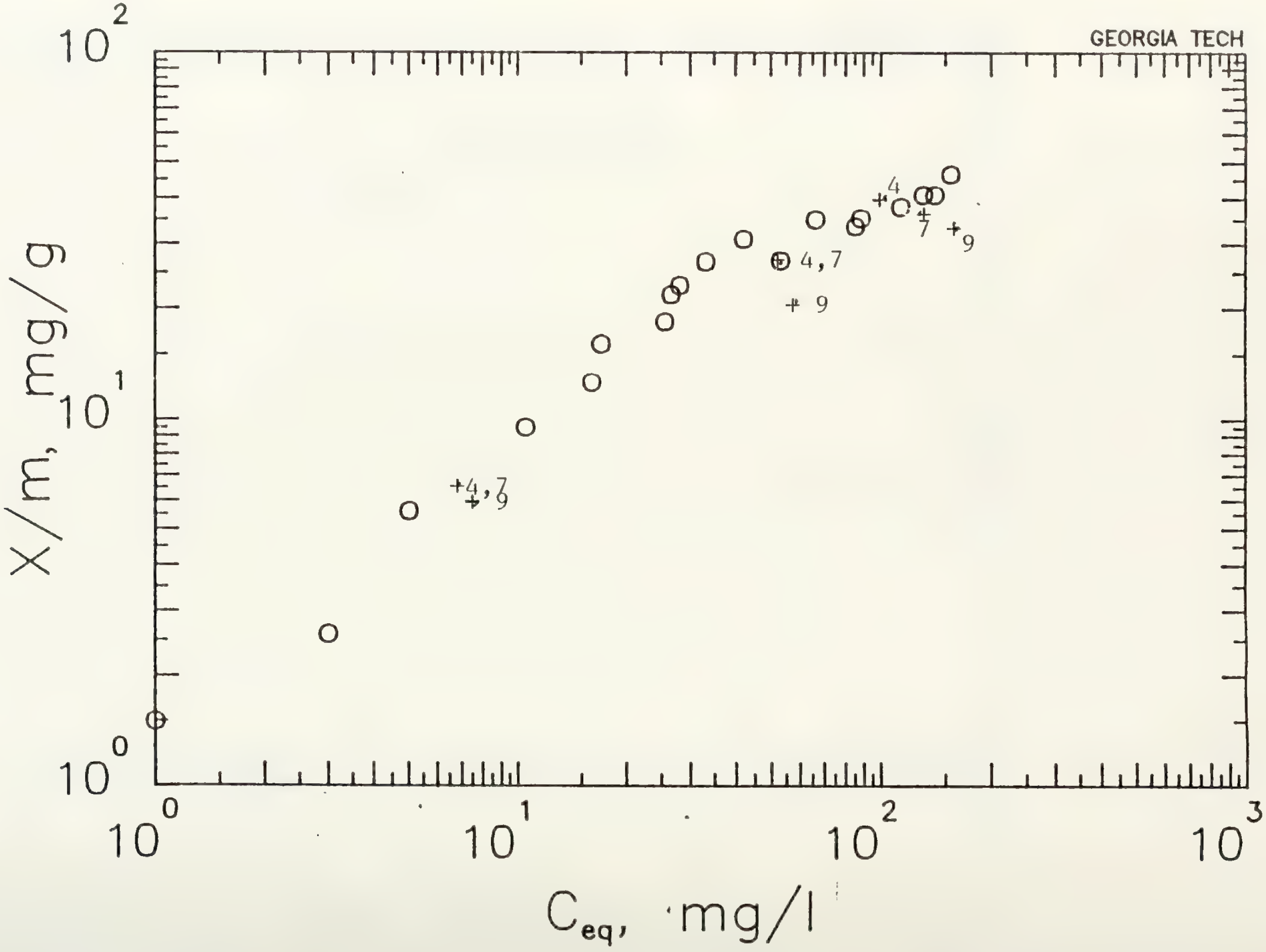


Figure 12. pH Test for 5,5-Dimethylhydantoin

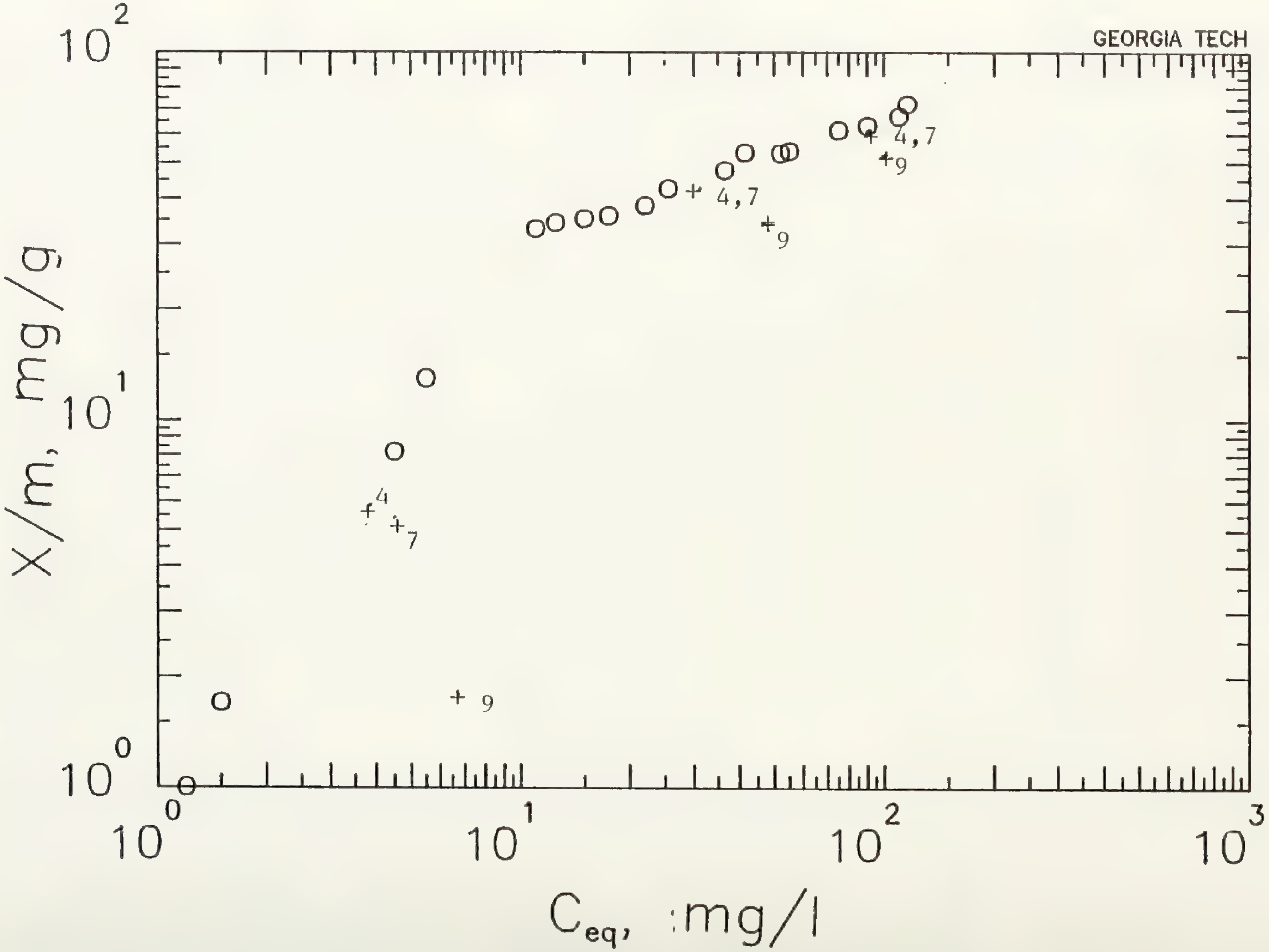


Figure 13. pH Test for 5-Ethyl-5-methylhydantoin

Table 7. Initial Conditions - Column Studies

hydantoin

temperature	28° C
influent concentration	55 mg/L
flow rate	20 ml/min
carbon	3.75 g
pH	5.6

5,5-dimethylhydantoin

temperature	28° C
influent concentration	45 mg/L
flow rate	20 ml/min
carbon	3.75 g
pH	5.6

5-ethyl-5-methylhydantoin

temperature	28° C
influent concentration	50.5 mg/L
flow rate	20 ml/min
carbon	3.75 g
pH	5.6

Table 7 (cont.)

hydantoin/5,5-dimethylhydantoin		
temperature		28° C
influent	hydantoin	40 mg/L
	5,5-dimethylhydantoin	59 mg/L
flow rate		20 ml/min
carbon		3.75 g
pH		5.6
hydantoin/5-ethyl-5-methylhydantoin		
temperature		28° C
influent	hydantoin	39.0 mg/L
	5-ethyl-5-methylhydantoin	50 mg/L
flow rate		20 ml/min
carbon		3.75 g
pH		5.6
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin		
temperature		27° C
influent	5,5-dimethylhydantoin	49.5 mg/L
	5-ethyl-5-methylhydantoin	54 mg/L
flow rate		20 ml/min
carbon		3.75 g
pH		5.6

Table 7 (cont.)

trisolute		
temperature		27° C
influent	hydantoin	41.5 mg/L
	5,5-dimethylhydantoin	38 mg/L
	5-ethyl-5-methylhydantoin	33 mg/L
flow rate		20 ml/min
carbon		3.75 g
pH		5.6
coal gasification wastewater		
temperature		27° C
influent		undiluted
flow rate		100 ml/min
carbon		30.0 g
pH		8.76

The results of the single solute column studies are depicted in Figures 14, 15, and 16. To provide a meaningful basis for comparison of the relative adsorption preferences of the three solutes, a calculation of the X/m values (amount of solute adsorbed per unit weight of carbon) reveals the following:

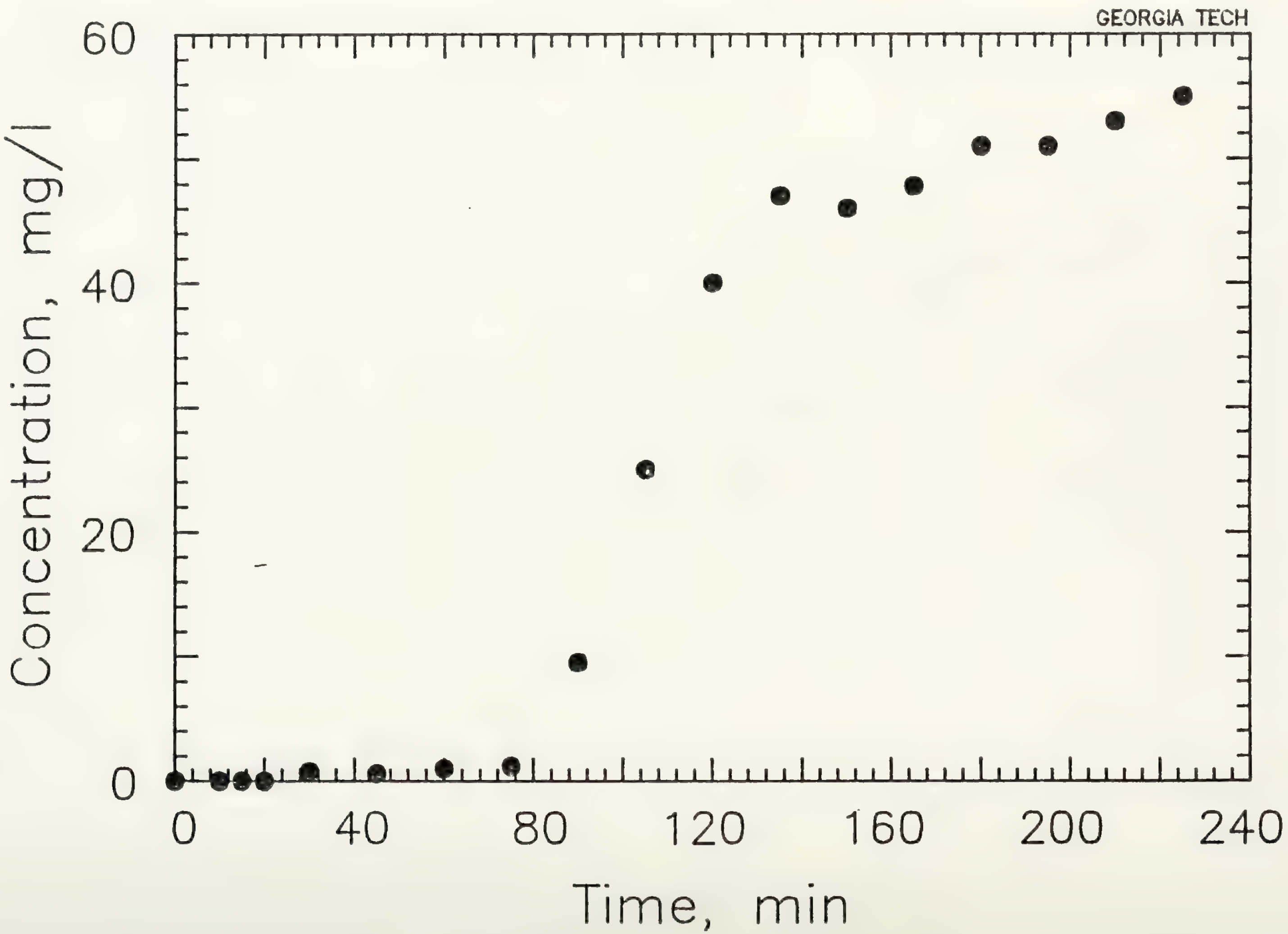


Figure 14. Breakthrough Curve for Hydantoin

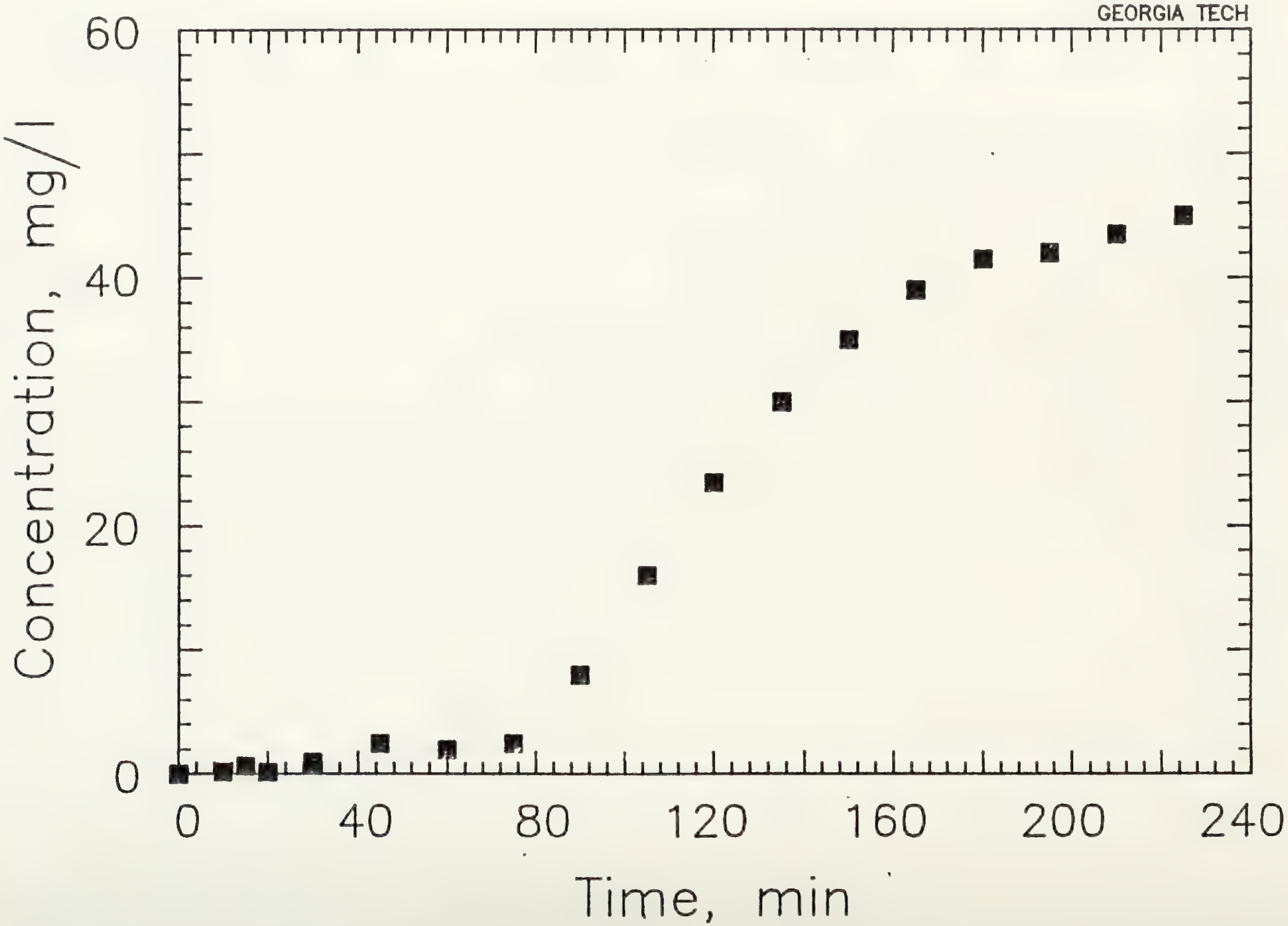


Figure 15. Breakthrough Curve for 5,5-Dimethylhydantoin

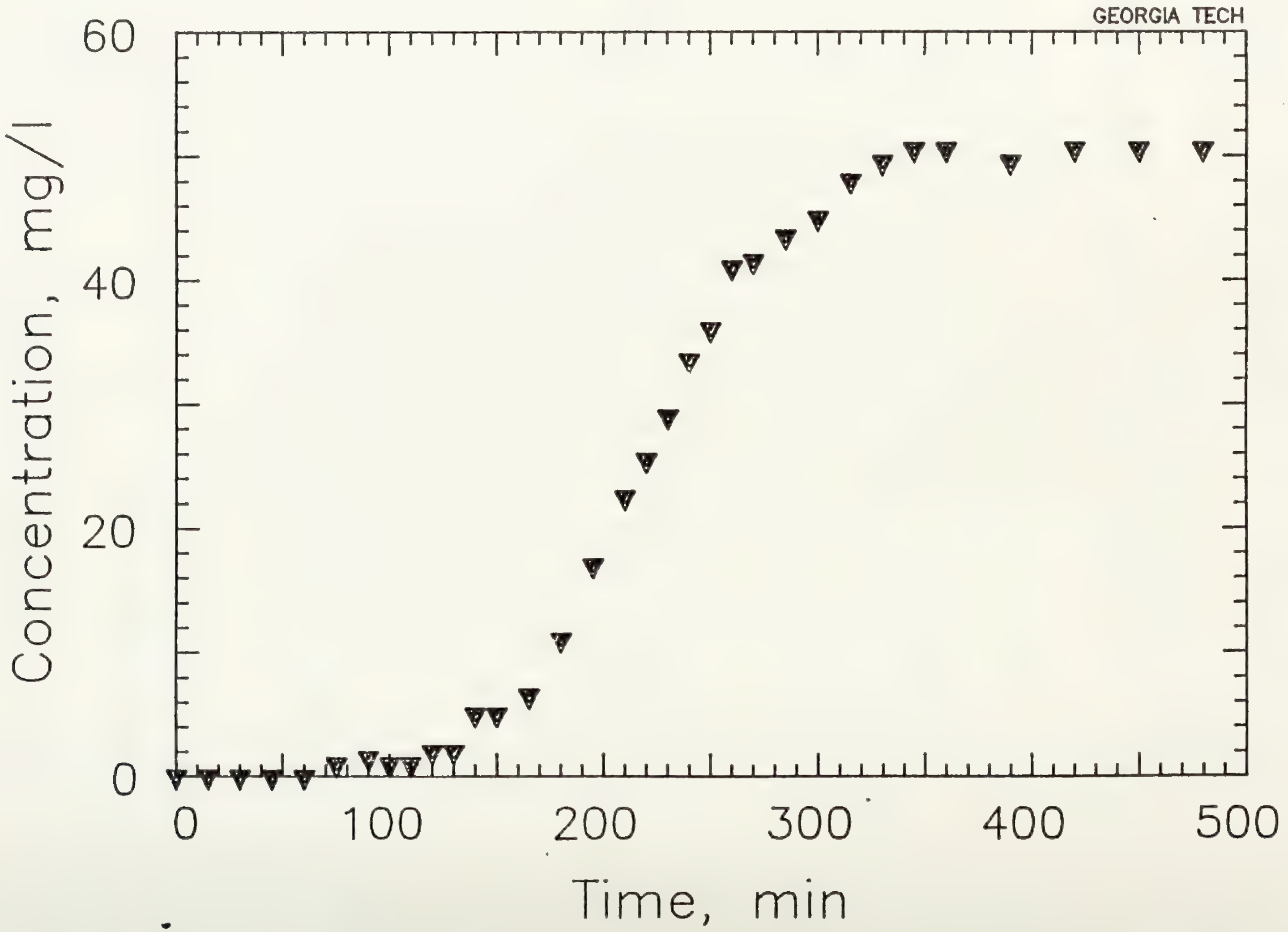


Figure 16. Breakthrough Curve for 5-Ethyl-5-methylhydantoin

Table 8. Single Solute Column X/m Values

hydantoin	41.3 mg/g
5,5-dimethylhydantoin	31.1 mg/g
5-ethyl-5-methylhydantoin	61.0 mg/g

The X/m value for hydantoin is slightly higher than expected. However, if the X/m value of 41.3 mg/g with a C_{eq} of 55 mg/L is plotted on the single solute isotherm for hydantoin (Figure 8), it will be seen to be within experimental error. The X/m values for the other two solutes plot directly on the single solute curves (Figures 9 and 10). From the single solute column studies, it is readily apparent that 5-ethyl-5-methylhydantoin is more strongly adsorbed than the other two adsorbents.

More vivid evidence for the various affinities of the carbon for the different solutes was provided by the bisolute and trisolute breakthrough curves which are shown in Figures 17, 18, 19, and 20.The calculated X/m values for the bisolute and trisolute breakthrough curves are shown in Table 9.

Table 9. Bisolute and Trisolute Column X/m Values

hydantoin/5,5-dimethylhydantoin	
hydantoin	21.0 mg/g
5,5-dimethylhydantoin	36.0 mg/g

Table 9 (cont.)

hydantoin/5-ethyl-5-methylhydantoin	
hydantoin	19.0 mg/g
5-ethyl-5-methylhydantoin	57.0 mg/g
5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin	
5,5-dimethylhydantoin	22.0 mg/g
5-ethyl-5-methylhydantoin	58.0 mg/g
trisolute	
hydantoin	17.0 mg/g
5,5-dimethylhydantoin	17.0 mg/g
5-ethyl-5-methylhydantoin	33.0 mg/g

Although from Figure 17 it appeared that the affinity of the carbon for hydantoin and 5,5-dimethylhydantoin was equal, the X/m values for the hydantoin/5,5-dimethylhydantoin in Table 9 showed that the carbon had a higher capacity for 5,5-dimethylhydantoin over hydantoin. The bisolute curve hydantoin/5-ethyl-5-methylhydantoin (Figure 18) showed a stronger adsorption of 5-ethyl-5-methylhydantoin by the fact that hydantoin was displaced from the activated carbon during the column test. This was demonstrated by the effluent concentration of the hydantoin becoming greater than the influent concentration. This was caused by all hydantoin in

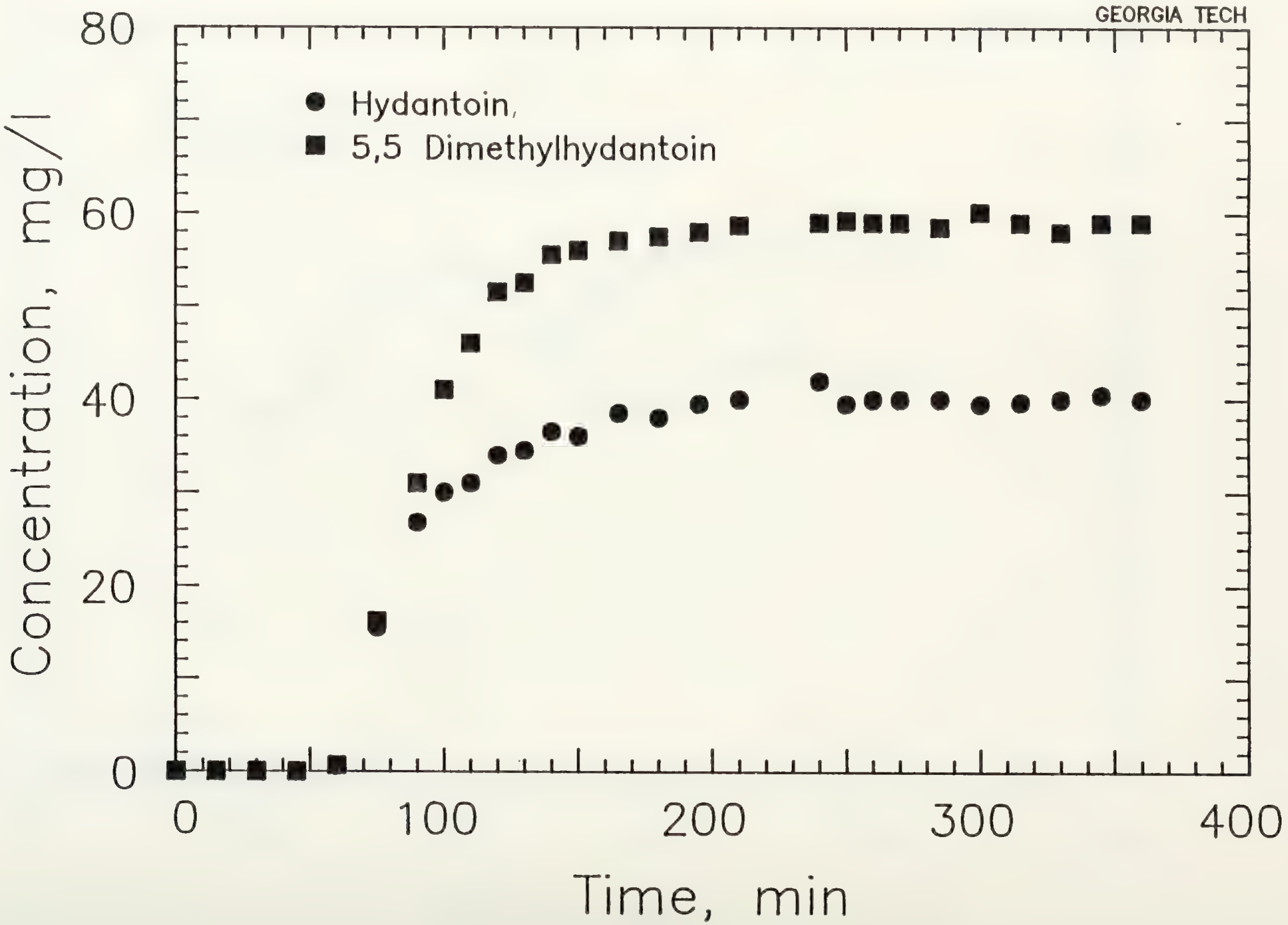


Figure 17. Bisolute Breakthrough for Hydantoin/5,5-Dimethylhydantoin

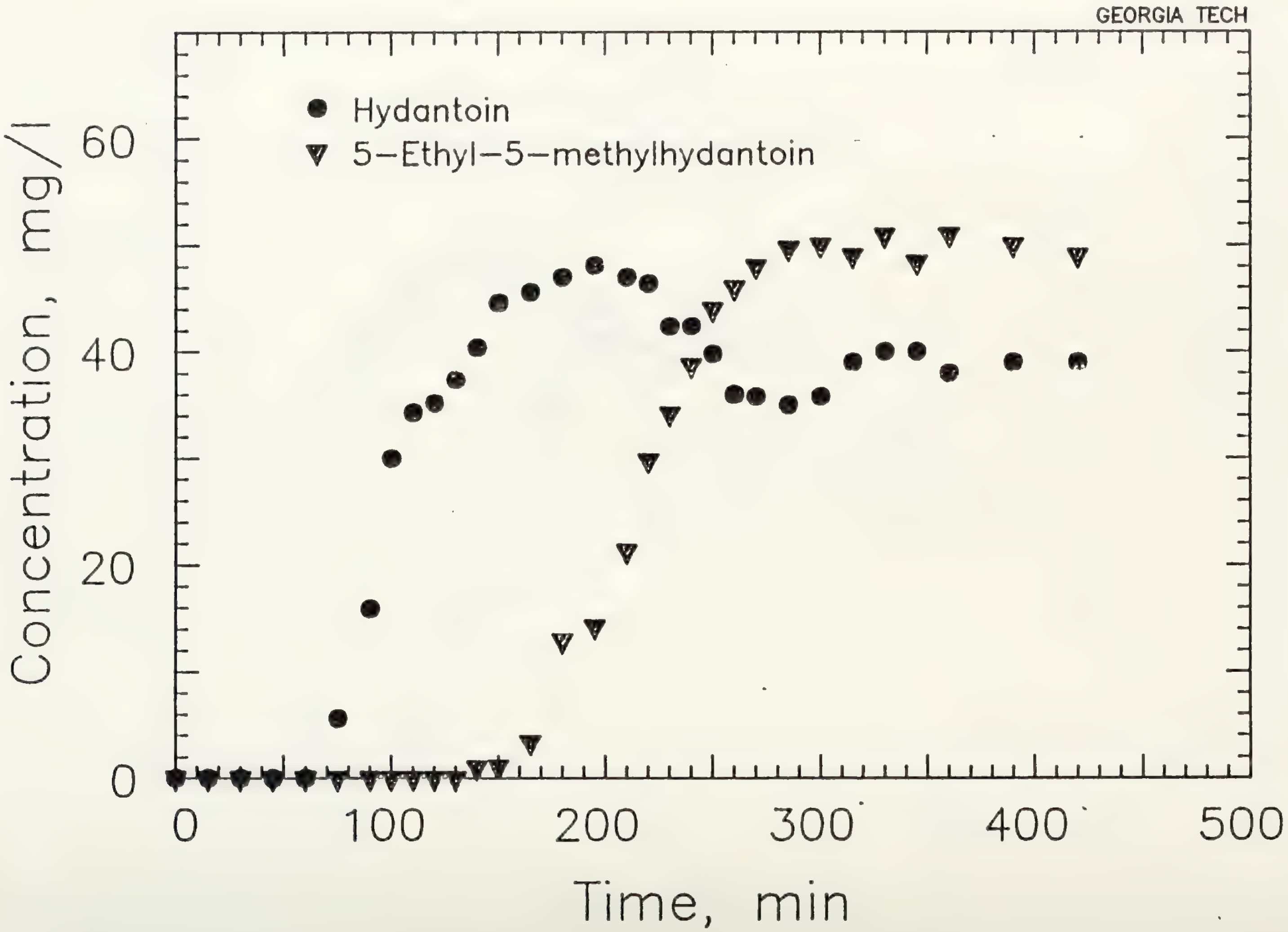


Figure 18. Bisolute Breakthrough Curve for Hydantoin/5-Ethyl-5-methylhydantoin

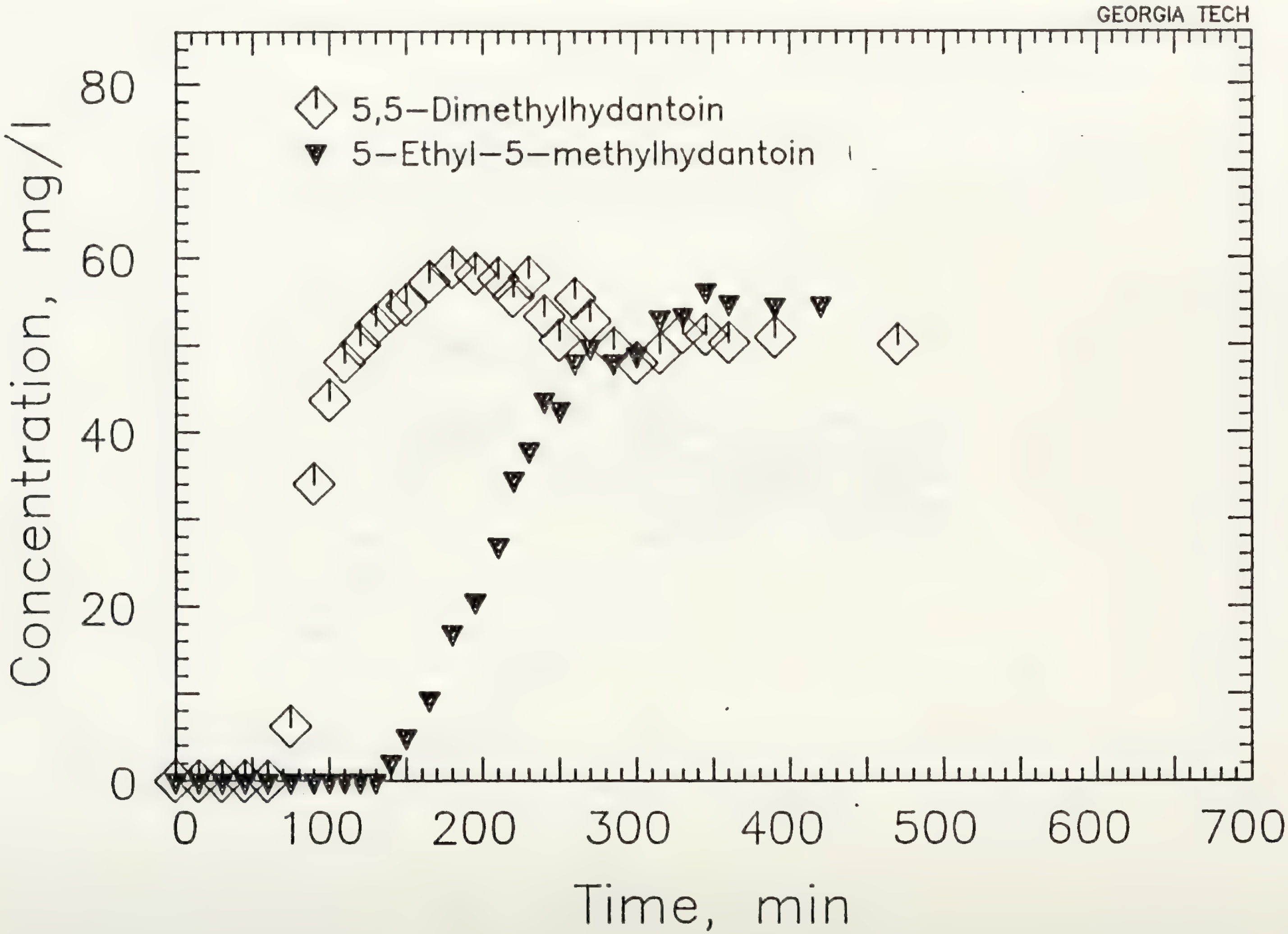


Figure 19. Bisolute Breakthrough Curves for 5,5-Dimethylhydantoin/

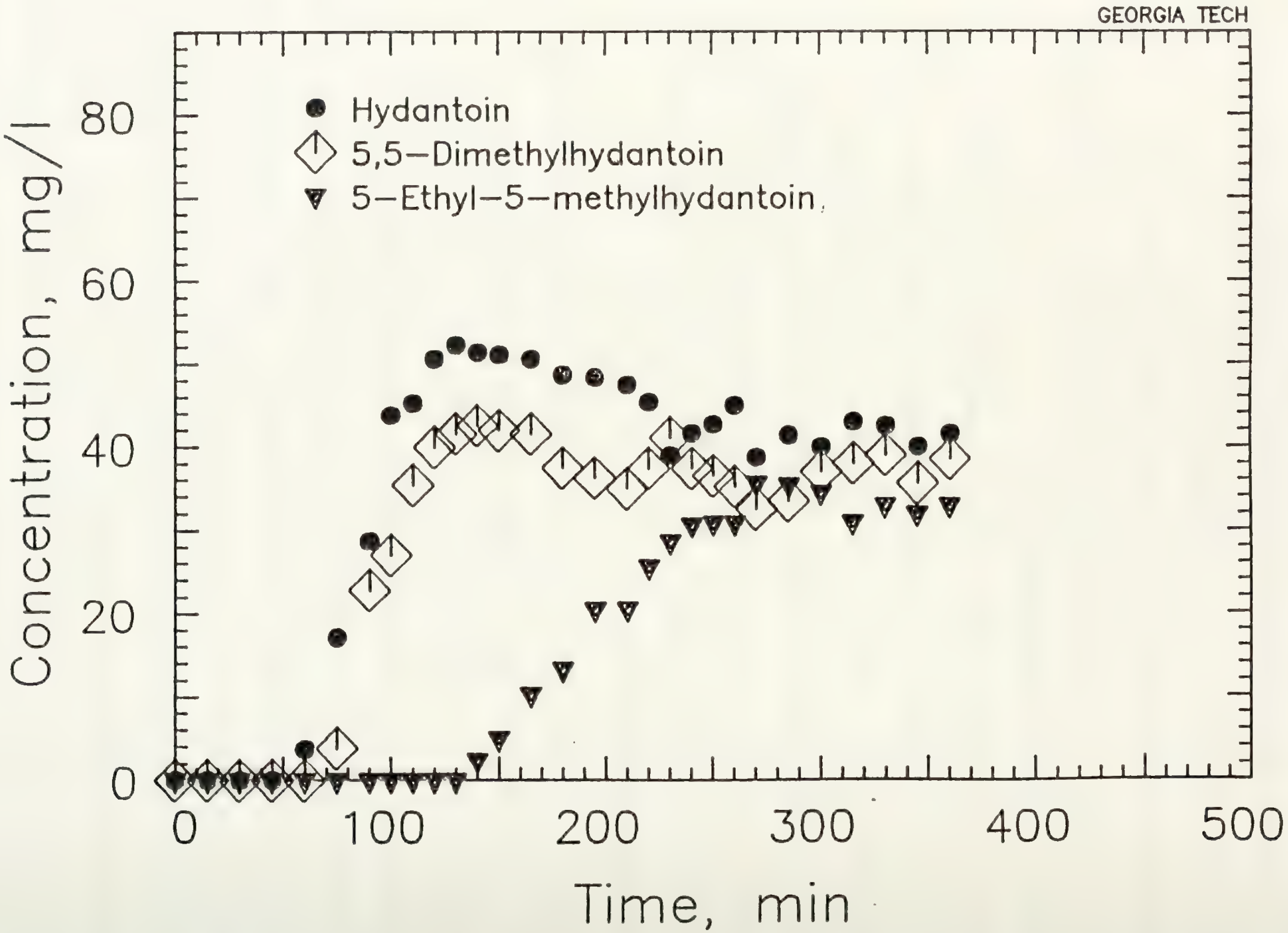


Figure 20. Trisolute Breakthrough Curve

the influent passing through the column unadsorbed, and additional hydantoin was added to the effluent due to displacement from the carbon through competition with the more strongly adsorbed 5-ethyl-5-methylhydantoin. A comparison of the X/m values in Table 9 also showed that 5-ethyl-5-methylhydantoin was more strongly adsorbed than hydantoin. The bisolute curve 5,5-dimethylhydantoin/5-ethyl-5-methylhydantoin again showed a displacement of the more weakly adsorbed solute, 5,5-dimethylhydantoin, by the more strongly adsorbed 5-ethyl-5-methylhydantoin. The X/m values in Table 9 verify that the carbon has a higher adsorption capacity for the 5-ethyl-5-methylhydantoin over the 5,5-dimethylhydantoin.

A double displacement effect ocurred in the trisolute breakthrough curve. The most strongly adsorbed 5-ethyl-5-methylhydantoin displaced both hydantoin and 5,5-dimethylhydantoin from the carbon as can be seen in Figure 20. From Table 9, the X/m values for hydantoin and 5,5-dimethylhydantoin were equal while the carbon exhibited a much higher adsorption capacity for the 5-ethyl-5-methylhydantoin.

Overall, a review of theresults in Table 9 show an adsorption preference of 5-ethyl-5-methylhydantoin > 5,5-dimethylhydantoin > hydantoin.

The breakthrough curves for the actual coal gasification wastewater is shown in Figure 21. Immediately following is the

breakthrough curve for total organic carbon for the wastewater (Figure 22). The amount of carbon used in the column was 30 grams with a flow rate of 100 ml/min. From Figure 21, the least strongly adsorbed 5,5-dimethylhydantoin broke through first between 10 and 15 minutes from the start of the test followed by 5-ethyl-5-methylhydantoin breaking through between 15 and 20 minutes. 5,5-Dimethylhydantoin reached carbon exhaustion at 1977 mg/l within 10 minutes of initiating breakthrough. 5-Ethyl-5-methylhydantoin reached influent concentration after 55 minutes. Phenol did not appear until 85 minutes from the test start and slowly reached exhaustion at 165 minutes. A slight displacement of solute occurred with 5,5-dimethylhydantoin being displaced by the 5-ethyl-5-methylhydantoin. Also, slight displacement of the 5-ethyl-5-methylhydantoin by the phenol occurred.

The X/m values for each of the solutes measured in the coal gasification wastewater are shown in Table 10.

Table 10. Coal Gasification Wastewater X/m Values

5,5-dimethylhydantoin	95.5 mg/g
5-ethyl-5-methylhydantoin	41.8 mg/g
phenol	64.5 mg/g

At face value, it appears that 5,5-dimethylhydantoin was more strongly adsorbed than phenol in the coal gasification

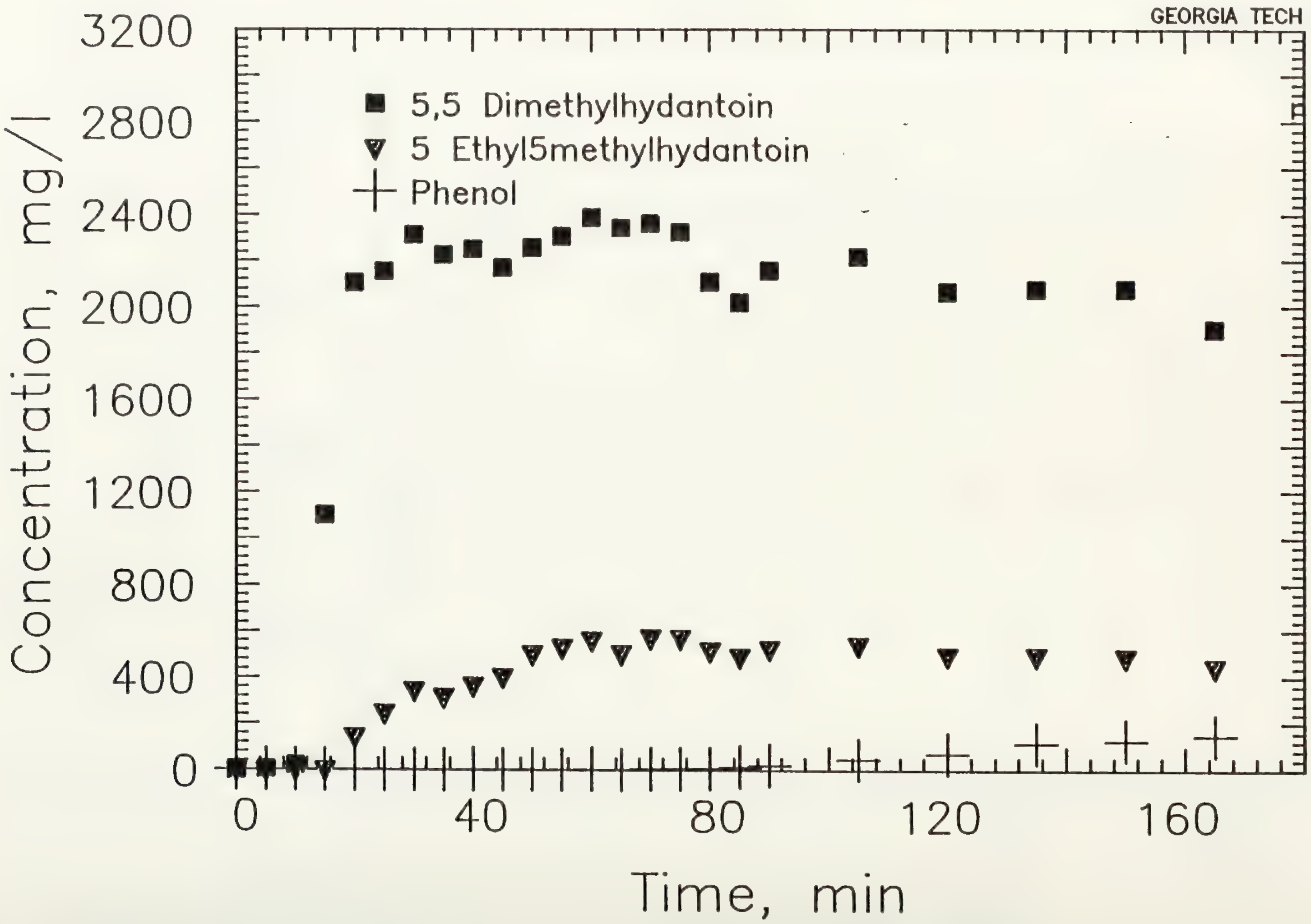


Figure 21. Breakthrough Curves for Coal Gasification Wastewater

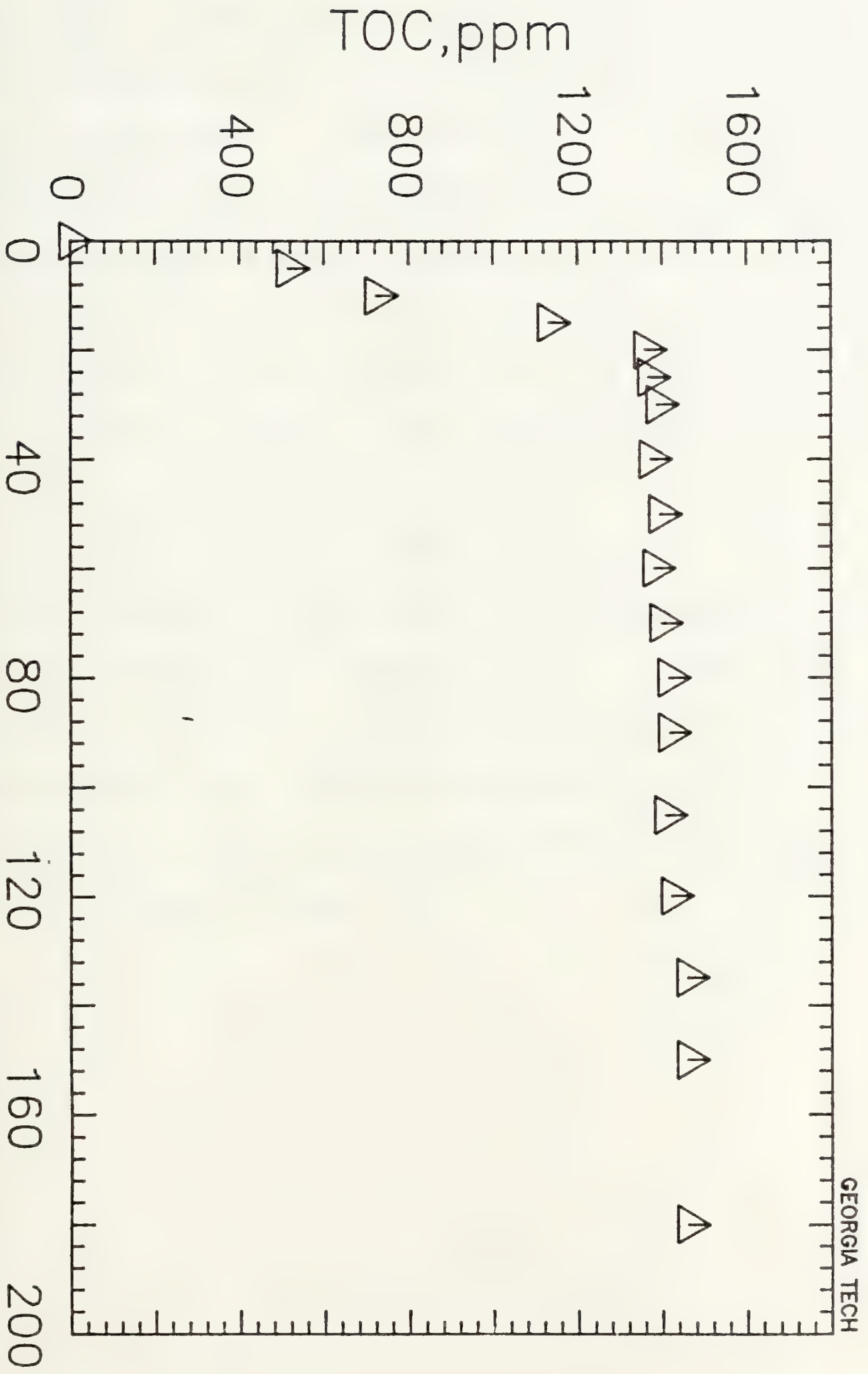


Figure 21. TOC Breakthrough Curve for Coal Gasification Wastewater

wastewater due to its higher X/m value in Table 10. However, the higher X/m value is due to the concentration of the 5,5-dimethylhydantoin being two orders of magnitude higher than the phenol concentration. A more definitive determination of adsorption preferences can be obtained from the coal gasification wastewater breakthrough curves where phenol was the last compound to show in the column effluent, and where phenol displaced both 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin from the carbon. Phenol was apparently the most strongly adsorbed compound.

A comparison of the X/m values found in Table 10 with the single solute isotherm curves for 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin (Figures 9 and 10) reveals that the X/m values found in the column study for coal gasification wastewater were significantly lower than the expected X/m values for the pure single solute system given equivalent solute concentrations. A comparison follows in Table 11.

Table 11. Comparison of X/m Values for Coal Gasification Wastewater and Pure Solutes

5,5-dimethylhydantoin	
concentration	1977 mg/L
pure X/m	145 mg/g
wastewater X/m	95.5 mg/g
5-ethyl-5-methylhydantoin	
concentration	456 mg/L
pure X/m	120 mg/g
wastewater X/m	41.8 mg/g

Hydantoin could not be shown since the gas chromatographic columns used could only retain 5,5-dimethylhydantoin, 5-ethyl-5-methylhydantoin, phenol and cresols. Other compounds existed in the wastewater to provide an interference in using the TOC analyzer to provide an indirect reading of the hydantoin concentration. Therefore, hydantoin concentration could not be determined.

The TOC breakthrough curve is interesting since it shows that the wastewater contains some substances that are apparently not readily adsorbed on activated carbon. This is shown by noting that some TOC broke through the carbon column immediately from

the start of the test. It is assumed that the compounds that were not adsorbed were large molecules that could not physically fit inside the carbon pore.

6. Summary and Conclusions

The batch kinetic tests for single solutes demonstrated that the kinetics of adsorption for hydantoin, 5,5-dimethylhydantoin, and 5-ethyl-5-methylhydantoin were very rapid with most of the adsorption occurring in the first 20 minutes.

The relative strength of adsorption of the three solutes was established by the single solute, bisolute, and trisolute isotherm points as follows: hydantoin < 5,5-dimethylhydantoin < 5-ethyl-5-methylhydantoin. This relationship held true regardless of the relative concentration of each solute with respect to the other as demonstrated by the coal gasification wastewater breakthrough curve. Even though 5,5-dimethylhydantoin was present in concentrations of 1977 mg/L, 5-ethyl-5-methylhydantoin at concentrations of 456 mg/L was still able to displace it from the carbon, and was therefore more strongly adsorbed. The bisolute and trisolute isotherm points also demonstrated competitive effects between the solutes relative to their respective strengths of adsorption. The X/m values for each adsorbate was

markedly reduced by the presence of a second and third solute. Within a given weight of activated carbon, there was a finite number of adsorption sites that could be utilized by the three adsorbates. Although hydantoin was the least strongly adsorbed solute, it was not totally desorbed by eigher the 5,5-dimethylhydantoin or the 5-ethyl-5-methylhydantoin, and 5,5-dimethylhydantoin was not totally desorbed by the 5-ethyl-5-methylhydantoin. Since the X/m values for the less strongly adsorbed compounds are lower than the corresponding X/m value for the single solute, it is obvious some displacement of the weaker by the more strongly adsorbed compoumd occurs. However, since an apparently large percentage of the weaker adsorbate, hydantoin, would still be adsorbed on the carbon after the most strongly adsorbed compound, 5-ethyl-5-methylhydantoin, had reached equilibrium, adsorption sites on the carbon appear to have a site specific affinity for one particular solute over the other.

The characteristics of the various adsorbates could be the leading cause of the adsorption preferences encountered. The difference in molecular structure of the three solutes was the presence of the alkyl groups or hydrogen bonded to the C(5). Hydantoin had no alkyl groups and was the most weakly adsorbed. 5-Ethyl-5-methylhydantoin had the largest molecular weight functional groups and was the most strongly adsorbed. 5,5-Dimethylhydantoin was in an intermediate position of adsorption strength.

Examples of adsorption strength based upon functional groups attached to the solute molecules were previously found by Belfort (1979).

The pH adjusted isotherm points within the high, mid-range, and low-range for each single solute isotherm conclusively showed that at a pH of 4 and 7, the X/m values were within experimental error of the isotherm curve. At pH 9, however, the X/m value was much lower. Therefore, at a pH of 9, the amount of solute adsorbed per unit weight of carbon is singificantly reduced.

The X/m values for the single solute breakthrough curves were either directly on or within experimental error of the X/m value for an equivalent solute concentration on the pure solute breakthrough curves. This phenomena enhances the probability that the single solute isotherms are accurate.

For the bisolute and trisolute curves, the X/m values demonstrated the adsorption preference of the activated carbon for the three adsorbates. From Table 9, it is obvious that 5,5-dimethylhydantoin is more strongly adsorbed than hydantoin from the hydantoin/5,5-dimethylhydantoin X/m values, and from the trisolute X/m values, that 5-ethyl-5-methylhydantoin is more strongly adsorbed than both of the other two adsorbates. Also, by observing the solute displacements which occurred on the actual bisolute and trisolute breakthrough curves (Figures 17 through 20), a relative adsorption preference can be observed.

The coal gasification wastewater breakthrough curves (Figure 21) with its associated X/m values (Table 10) yielded interesting results. A comparison of the X/m values for the coal gasification wastewater and pure solutes for equivalent solute concentrations (Table 11) showed significant reductions in the X/m values in the wastewater. The adsorption of 5,5-dimethylhydantoin was reduced by 34% and that of 5-ethyl-5-methylhydantoin was reduced 65% from the adsorption that would be expected in a pure solute system. The probable reasons for the reduction in adsorption capacity are twofold: (1) the increase in pH from 5.6 in pure systems to 8.76 in the actual wastewater, and (2) competition between the various solutes in the wastewater. From Figures 11, 12, and 13, it was shown that at a pH of 9, the amount of pure solute adsorbed on the carbon was reduced. Since the wastewater has a pH of 8.76, it is probable that the pH had an effect in reducing the X/m values for the wastewater. In addition, from the bisolute and trisolute isotherm points (Figures 8, 9, and 10) it was demonstrated that competition between the solutes will reduce the amount of hydantoins that will be adsorbed on activated carbon. In the coal gasification wastewater, the hydantoins were in competition with phenol (which was more strongly adsorbed) which would reduce the X/m values for the hydantoins. It is probable that both conditions contributed to a reduction in the amount of hydantoins

adsorbed in the wastewater in comparison to the pure solute systems.

From the carbon adsorption studies, it is apparent that hydantoins are poorly adsorbed by activated carbon. Based upon an X/m value of 95.5 mg/g for 5,5-dimethylhydantoin (1977 mg/L) in coal gasification wastewater, in order to reduce the 5,5-dimethylhydantoin by 50% (1 g/L), the amount of carbon required is 10.2 g per liter of wastewater processed. This equates to approximately 42.5 Tons/mgal which is an extremely high usage rate. Also, from the TOC breakthrough curve (Figure 22), the rapid breakthrough of TOC from the beginning of the test indicates that some compounds within the wastewater are not adsorbed by the activated carbon at all. Therefore, adsorption by activated carbon does not appear to be a viable alternative in the removal of hydantoins from the wastewater.

Since hydantoins are not readily adsorbed on carbon, a non-polar adsorbent, the possibility exists that a polar adsorbent may be more effective in removal of hydantoins from the wastewater. Since hydantoins are principally in the form of cationic species below a pH of 9.0-9.2, an anionic resin may be more efficient in the removal of hydantoins. Further study would be required to verify this theory.

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